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SURVEY OF INDUSTRIAL PROCESSING DATA

TASK I - HEXACHLOROBENZENE AND HEXACHLOROBUTADIENE POLLUTION FROM CHLOROCARBON PROCESSING

Midwest Research Institute

PREPARED FOR

Environmental Protection Agency

June 1975

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JUNE 1975

FINAL REPORT

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
4TH AND M STREETS, S.W.
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SURVEY OF INDUSTRIAL PROCESSING DATA

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JUNE 1975

PREFACE

This report presents the results of the Task I study of a project entitled "Survey of Industrial Processing Data." Task I, "Hexachlorobenzene and Hexachlorobutadiene Pollution From Chlorocarbon Processes," was performed by Midwest Research Institute (MRI) under Contract No. 68-01-2105 for the Office of Toxic Substances of the U.S. Environmental Protection Agency. The MRI Project No. was 3822-C.

Task I was conducted during the periods 27 June to 15 November 1973 and 1 March to 7 October 1974 with final revisions made in April 1975. This program was under the supervision of Dr. E. W. Lawless, Head, Technology Assessment Section. Mr. C. E. Mumma, Senior Chemical Engineer, served as project leader. Other MRI personnel who contributed significantly to this study included: Mr. G. Kelso, Assistant Chemical Engineer; Mr. G. Cooper, Assistant Chemist; Mr. J. Edwards, Assistant Chemist; and Ms. Cassandra Collins, Junior Chemist. Dr. A. F. Meiners, Principal Chemist and Dr. Harold Orel, Consultant on Technical Writing, reviewed drafts of this report and provided technical and editorial assistance.

This final report for Task I was prepared by Mr. Mumma and Dr. Lawless.

Task II of this study is on brominated biphenyl compounds; it is the subject of a separate report.

Approved for:

MIDWEST RESEARCH INSTITUTE

H. M. Hubbard, Director
Physical Sciences Division

10 July 1975

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I. INTRODUCTION

Hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD) have aroused concern because of technical publications and reports by the news media that these substances have been found as trace contaminants in the environment and, in rare instances, in certain food supplies in the U.S.

During the summer of 1972, government inspectors identified HCB in domestic meat and poultry supplies. HCB residues have been observed in animal tissues from several widely separated locations[1] including Darrow, Louisiana; Dimmitt, Texas; Phoenix, Arizona; and Westmoreland, California. The Food and Drug Administration is investigating the extent of HCBD contamination in various domestic food supplies.

Because of these reports of HCB-HCBD contamination, and concern about the toxicity of these substances, the Office of Toxic Substances, EPA, directed MRI to undertake this study. Much of the effort was designed to identify possible sources and effects of HCB and HCBD. In addition to HCB and HCBD, three other chemical products were initially selected for investigation because it was considered likely that HCB and/or HCBD would escape into the environment as a result of their production. These three chemicals were hexachloroethane, pentachlorophenol, and pentachlorobenzene.

As the investigations of these five products progressed MRI identified, through discussions with industry representatives and surveys of technical literature for chemical processing, a number of additional chemical substances whose production was considered to be potential sources of environmental contamination by HCB and/or HCBD. During discussions with EPA representatives, it was mutually agreed that 18 additional chemicals should be included in the project investigations because they also represent a proven or theoretical source of HCB and/or HCBD. Thus, a total of 23 chemicals and chemical product industries were of interest; they were:

* Hexachlorobenzene
* Hexachlorobutadiene
* Hexachloroethane
* Pentachlorophenol
* Pentachlorobenzene
* Chlorine
* Sodium chlorate
* Sodium metal
* Carbon tetrachloride
* Perchloroethylene
* Trichloroethylene
* Vinyl chloride monomer
* Synthetic rubber (chloroprene)
* Atrazine
* Propazine
* Simazine
* Pentachloronitrobenzene
* Dacthal®
* Mirex
* Maleic hydrazide
* Hexachlorocyclopentadiene
* Chlorinated naphthalenes
* Chlorinated biphenyls

The scope of work included:

1. Identification of production sites and production volumes.

2. Description of manufacturing processes and environmental and health aspects.

3. Characterization of waste disposal methods.

4. Identification of commercial uses for chemical products.

5. Recommendations concerning selected plant monitoring sites.

The following sections of this report discuss methodology, results obtained in each major assignment, and an evaluation conducted to identify those chemical plants at which monitoring should be conducted. The appendices provide further information on: manufacturing sites and production and import volumes of the 23 substances; a written inquiry sent to nine manufacturers; and the rationale for the process used to identify the plants to be monitored.

The subject index included at the end of this report provides, for each chemical of interest, a notation of the first page number for the discussion of that chemical in each major report section.

This study of HCB and HCBD was Task I under this contract. Task II of this program, a study of brominated biphenyl compounds, will be completed in June 1975 and will be the subject of a separate report.

II. SUMMARY

On 5 July 1973, the Office of Toxic Substances of the U.S. Environmental Protection Agency authorized Midwest Research Institute (MRI) to initiate a project entitled "Survey of Industrial Processing Data" (EPA Contract No. 68-01-2105). Primary objectives of this project were to collect information on environmental aspects of U.S. production and use of specific toxic substances, to be designated by EPA, and to organize this information into a form which will assist EPA in assessing their environmental impacts. The present study was made to help the EPA evaluate the potential for environmental contamination by hexachlorobenzene (C_6Cl_6; abbreviated HCB), and hexachlorobutadiene (C_4Cl_6; abbreviated HCBD). This study was conducted during the period of 27 June 1973 to 7 October 1974.

Information acquisition and evaluation activities were designed to identify proven or potential sources of HCB and HCBD and the environmental and health effects of these substances. In addition to HCB and HCBD, this study included 21 other domestically produced chemicals which were either known sources of HCB and/or HCBD or theoretically capable of generating these substances as by-products, waste materials, or impurities in a commercial product. These additional chemicals were identified through discussions with EPA, manufacturer's representatives and surveys of technical literature; they were:

- Chlorine
- Vinyl chloride monomer
- Carbon tetrachloride
- Perchloroethylene
- Trichloroethylene
- Sodium chlorate
- Synthetic rubber (chloroprene)
- Atrazine
- Hexachlorocyclopentadiene
- Pentachlorophenol
- Chlorinated biphenyls
- Simazine
- Chlorinated naphthalenes
- Propazine
- Maleic hydrazide
- Pentachloronitrobenzene
- Pentachlorobenzene
- Dacthal®
- Mirex
- Hexachloroethane
- Sodium metal

The scope of the study for each of these chemicals included identification of production sites and volumes, descriptions of manufacturing processes and environmental and health aspects, description of waste disposal methods, and identification of commercial uses for these products. An important goal was the recommendation of specific plant sites that should be monitored by EPA to determine if they were sources of significant discharges or emissions of HCB and/or HCBD into the environment.

Sources of the project team's information included several standard reference publications, technical literature for the chemical process industry, telephone and letter inquiries to producers, trade organizations and government agencies, and a written questionnaire submitted to nine selected chemical producers.

The major findings in this study are briefly described in the following subsections.

1. Chemical production volumes, sites and manufacturers: Production data for the 23 chemicals of interest are presented in Table S-1.

The production rates, sites, and manufacturers range from none for HCBD to nearly 20 billion pounds per year, 65 sites and 32 manufacturers for chlorine. Production sites for chemicals of interest are heavily concentrated in Louisiana, Texas, and Alabama. Chlorine manufacture represents the most widely dispersed operations, with plants in 23 states. In contrast, each of the pesticide chemicals listed is produced at only a few sites (five or less).

2. Manufacturing processes that produce HCB or HCBD: Neither HCB nor HCBD appear to be direct products of a commercial manufacturing process--although synthesis routes are known--and both are normally obtained in commercial quantities as by-products. HCB is a specialty chemical reclaimed in domestic practice as a by-product of undisclosed (proprietary) chlorinated hydrocarbon processes. In 1974, there was only one active domestic HCB producer. Industry sources report that environmental contamination by HCB does not occur in these manufacturing operations, since all of the by-product HCB is recovered and sold. HCBD has been recovered domestically as a by-product in some chlorinated hydrocarbon processes (e.g., perchloroethylene production). In 1974, no HCBD was produced in the United States, but 200,000 to 500,000 lb were reported to be imported the same year.[2]

In the study of manufacturing processes for the 21 other selected chemicals, MRI identified 11 that are known to produce HCB and/or HCBD as by-products, waste components, or impurities; they are:

* Chlorine
* Carbon tetrachloride
* Perchloroethylene
* Trichloroethylene
* Dacthal®
* Atrazine
* Propazine
* Simazine
* Pentachlorobenzene
* Pentachloronitrobenzene
* Mirex

TABLE S-1

U.S. CHEMICAL PRODUCTION VOLUMES, SITES, AND MANUFACTURERS

Chemical[a]	Total Production Volume (10^6 lb/year)[b]	Total Production Sites in U.S.[b]	Number of Manufacturers[f]
Chlorine	19,736[c]	65	32
Vinyl chloride monomer	5,089	16	12
Carbon tetrachloride	997	11	6
Perchloroethylene	734	10	7
Sodium chlorate	428	15	10
Trichloroethylene	427	5	5
Synthetic rubber (chloroprene)	396	6	4
Atrazine	100	2	1
Hexachlorocyclopentadiene	50[d]	4	2
Pentachlorophenol	49	4	4
Chlorinated biphenyls	38.6	1	1
Simazine	8	1	1
Maleic hydrazide	8[d]	4	4
Chlorinated naphthalenes	< 5[d]	1	1
Propazine	4	1	1
Pentachloronitrobenzene	3[d]	2	1
Dacthal®	2[d]	1	1
Mirex	< 1[d]	1	1
Hexachlorobenzene	0.7[d]	3	3
Hexachloroethane	0.4	1	1
Sodium metal	0.15	5	3
Pentachlorobenzene	< 0.002[d]	6[g]	6
Hexachlorobutadiene	[e]	3[h]	2

---

[a] The chemicals are listed in descending order of total production volume.

[b] 1972 production volumes, except as otherwise noted (see Appendix A).

[c] Chlorine Institute Pamphlet No. 10, January 1974.

[d] MRI estimate. See Section III and Appendix A.

[e] No domestic production for commercial marketing (small amounts are imported).

[f] SRI Chemical Information Service, Chemical Economics Handbook, Stanford Research Institute (1974).

[g] Includes four plants which produce pentachlorobenzene as a by-product and two specialty chemical companies.

[h] All three sites are inactive.

HCB can be formed as a by-product in the production of chlorine gas by electrolysis of sodium chloride[3] in cells with carbon electrodes. Both HCB and HCBD can be formed as by-products or waste material in the manufacture of carbon tetrachloride, perchloroethylene, and trichloroethylene.[3] The only domestic producer of Dacthal® has reported (see Appendix B) that no HCBD is generated, that the product contains about 0.3% HCB, and that the process wastes contain about 84% HCB. The producer of atrazine, propazine, and simazine has reported (see Appendix B) that no HCBD is produced, but that each product and the related process waste materials contain measurable amounts of HCB. HCB can be formed as a by-product in the production of pentachlorobenzene.[4] Two pesticide products, pentachloronitrobenzene and mirex, are known to be contaminated with HCB.[5]

3. Evaluation of the HCB and HCBD pollution potential: An evaluation was made of the potential for environmental pollution by HCB and HCBD on the basis of the information obtained on the production and use of the 23 chemicals of interest. In this evaluation, MRI developed estimates of the probable quantities of HCB and HCBD generated as by-products, contaminants in products, or components of waste materials in each of the manufacturing processes and product industries.

The results, presented in Table S-2, show that production of three related industrial chemicals, carbon tetrachloride, perchloroethylene, and trichloroethylene, account for 89% of the HCB and more than 99% of the HCBD that are formed in the U.S. The perchloroethylene industry alone generates about 72% of the total HCB and 60% of the total HCBD. Chlorine and various pesticides (atrazine, propazine, simazine, Dacthal®, mirex, and pentachloronitrobenzene) generate about 10% of the total HCB. Vinyl chloride accounts for the remaining 1% of the HCB.

For the 11 chemical processes considered in Table S-2, the total HCB generated ranged from a low estimate of 2.4 million pounds to a high estimate of 4.9 million pounds in 1972. The total estimated HCBD ranged from about 7.3 to 14.5 million pounds.

4. Disposal methods for wastes containing HCB and/or HCBD: The chlorine industry uses sanitary landfill or high-temperature incineration methods. In the chlorinated hydrocarbon industries of interest (carbon tetrachloride, perchloroethylene, trichloroethylene, pentachlorobenzene and pentachloronitrobenzene), the disposal methods include landfill, incineration, and deep-well injection. Incineration is reported to be a highly effective disposal method in which practically all HCB and HCBD are destroyed. The landfill operations pose a potential air pollution hazard, since HCB is volatile in water vapor at low temperatures. Deep-well injection systems are undesirable since they may create geological fractures which can result in contamination of aquifers.

TABLE S-2

ESTIMATED TOTAL QUANTITY OF HCB AND HCBD CONTAINED IN U.S. INDUSTRIAL WASTES, BY-PRODUCTS, AND PRODUCTS IN 1972[a]

End-Products	HCB (000 lb)[b] High	HCB (000 lb)[b] Low	HCBD (000 lb)[b] High	HCBD (000 lb)[b] Low
Perchloroethylene	3,500	1,750	8,670	4,340
Trichloroethylene	450	230	3,000	1,500
Carbon tetrachloride	400	200	2,790	1,400
Chlorine	390	160	70	40
Dacthal®	100	80	0	0
Vinyl chloride	27	0	0	0
Atrazine, propazine, simazine	9	5	0	0
Pentachloronitrobenzene	6	3	0	0
Mirex	2	1	0	0
Total	4,884	2,429	14,530	7,280

---

[a] See Section V for description of waste disposal methods used.

[b] Rounded to nearest 10,000 lb--except for vinyl chloride, atrazine, propazine, simazine, pentachloronitrobenzene, and Mirex.

The pesticide process wastes of concern to this study (i.e., from production of atrazine, propazine, simazine, and Dacthal®) are disposed of by incineration.

5. Commercial uses of HCB, HCBD, and selected chemicals: A brief discussion of the use patterns for selected products, which are known to contain, or theoretically may contain, HCB and/or HCBD, follows.

Hexachlorobenzene: In 1972, the principal use for HCB was reported to be as a fungicide to control wheat bunt and smut fungi of other grains. The technical grade used in agriculture is reported to contain 98% hexachlorobenzene, 1.8% pentachlorobenzene, and 0.2% of 1,2,4,5-tetrachlorobenzene. Commercial formulations applied as dusts contain 10 to 40% hexachlorobenzene.[3/] Other applications include use as: additives for pyrotechnic compositions for the military; a porosity controller in manufacture of electrodes; chemical intermediates in dye manufacture and organic synthesis; and a wood preservative.

In 1974, a spokesman for the only domestic producer (Stauffer Chemical Company) reported that their entire HCB production capacity had been committed on a multiyear contract basis for use only as a peptizing agent in nitroso- and styrene-type rubber manufacture in automobile tire plants.

Hexachlorobutadiene: The largest domestic use for HCBD is for recovery of "snift" (chlorine-containing) gas in chlorine plants.[2/] This "snift" gas, which occurs at the liquefication unit, is cleaned by passing it through HCBD or carbon tetrachloride. HCBD is also used as a chemical intermediate in the manufacture of rubber compounds. It has been used as a fluid for gyroscopes and as a chemical intermediate to produce lubricants.

Chlorine: A detailed materials flow diagram was prepared to illustrate the utilization of chlorine values in various chemical processing operations, intermediates, and end products. This schematic (see page 99) shows all major compounds which use chlorine as a raw material. About 59% of the total chlorine produced is consumed in the manufacture of chlorinated hydrocarbons (acyclic and cyclic); these industries, as a group, have the highest potential for generation of by-product HCB and HCBD. This chlorine distribution diagram should be useful in any future studies of chlorinated hydrocarbons derived from these basic chemical industries.

Dacthal®: This product is a preemergence herbicide used for cotton, peanuts, and a variety of vegetables.

Atrazine, propazine, and simazine: Atrazine is a selective herbicide; the major use is for corn and sorghum crops. Less than 10% is used by industry.

Propazine is a preemergence herbicide used to control broadleaved and grassy weeds in millet, sorghum, and umbelliferous crops.

Simazine is a herbicide widely used to control broadleaf and grassy weeds in corn, citrus crops, deciduous fruits and nuts, established alfalfa, perennial grasses, and nursery plantings. It is also applied as a nonselective herbicide for vegetation control on noncropland.

Pentachlorobenzene: This chemical is produced largely as a captive intermediate for synthesis of specialty chemicals. The estimated total domestic sales in 1972 were less than 1 ton.

Pentachloronitrobenzene: This product is used as a soil fungicide to control diseases of cotton, potatoes, tomatoes, and peppers. The use of 20% pentachloronitrobenzene in dust also gives satisfactory results as a seed disinfectant against smut.

Mirex: This insecticide is used for the control of some species of ants, and most widely in the USDA's fire ant control program in the southeastern states. It has been used for control of cotton pests and some Hawaiian pineapple growers have used it to control mealy bugs and ants.

6. Environmental and health aspects of HCB and HCBD: The technical literature[3/] indicates that HCB is a hazard to man and to the environment. It appears to be readily dispersed through the atmosphere, is accumulated in food chains, and is highly resistant to chemical, biological, and physical degradation. Since HCB sublimes and is also volatile in water vapor at low temperatures, it can be widely distributed by air transport. In the U.S. it has been detected in poultry and meat from 20 states and in marine ecosystems. HCB has a very low acute toxicity by single-dose administration; e.g., 500 mg/kg interperitoneal was nonlethal in rats, and the oral lethal dose of a 15% suspension of HCB in female Japanese quail was above 1 g/kg.[3/] In contrast, the subacute or chronic toxicity can be significant; serious physiological damage apparently can result from repeated exposure of animals to small dosages of this chemical (see Section VII). The literature[3/] shows some data on the mortality rates for oral feeding of HCB to rats; for a 30-day feeding period with 10 rats, 30% mortality was observed at a dosage of 50 mg/kg/day and 60% mortality was reported for a dosage of 150 mg/kg/day.

HCBD is also a toxic substance and potentially hazardous environmental pollutant that is resistant to chemical degradation. HCBD has greater acute toxicity than HCB. Tests conducted by the Hazelton Laboratories (see Section VII), indicate that the acute oral LD_{50} of HCBD for male albino rats is 178 µl/kg of body weight, and that the acute dermal LD_{50} for albino rabbits is 1,780 µl/kg.

III. CONCLUSIONS AND RECOMMENDATION

The following conclusions are drawn on the basis of this study:

1. Production and processing of perchloroethylene, trichloroethylene, and carbon tetrachloride accounts for an estimated 89% of the HCB and 99% of the HCBD that are produced in the United States. Production of chlorine and certain pesticides accounts for most of the remaining HCB, with vinyl chloride monomer accounting for about 1%. The chlorine industry also accounts for a small portion of the total amount of HCBD.

2. A review of waste-disposal technology and of discussions with industry spokesmen indicates that one of the most effective and safest methods for disposing of wastes containing HCB and HCBD involves the use of a specially designed high-temperature incineration system. Use of such special incinerators is increasing. Some deep-well injection and landfilling disposal methods are still being used, but are not preferred methods.

3. HCB is a stable and potentially hazardous environmental pollutant, which is highly resistant to chemical, biological, and physical degradation. The single-dose acute toxicity is very low, but the subacute or chronic toxicity can be significant. HCBD is also a stable environmental pollutant, and has greater acute toxicity than HCB.

On the basis of our technical evaluation (see Section VIII), it is recommended that sampling and analysis (monitoring) be conducted at several plants known to be, or suspected of, discharging HCB and/or HCBD. Samples should be taken from each plant's emissions, effluents, soil, solid wastes, and products to characterize and quantify the types and levels of HCB and HCBD. By industry class, the recommended monitoring sites and the products produced there are as follows:

1. Perchloroethylene-trichloroethylene-carbon tetrachloride:

   * PPG Industry, Inc.; Lake Charles, Louisiana; perchloroethylene and trichloroethylene.

   * Vulcan Materials Company; Wichita, Kansas; carbon tetrachloride and perchloroethylene.

   * Vulcan Materials Company; Geismar, Louisiana; carbon tetrachloride and perchloroethylene.

   * E. I. du Pont de Nemours and Company, Inc.; Corpus Christi, Texas; carbon tetrachloride.

2. Chlorine:

   * Kaiser Aluminum and Chemical Corporation; Gramercy, Louisiana; diaphragm cell operation.

   * Olin Corporation; McIntosh, Alabama; mercury cell operation.

3. Atrazine, propazine, simazine:

   * Ciba-Geigy Corporation; St. Gabriel, Louisiana; atrazine, propazine, and simazine.

4. Vinyl chloride monomer:

   * PPG Industry, Inc.; Lake Charles, Louisiana.

5. Pentachloronitrobenzene:

   * Olin Corporation; McIntosh, Alabama.

6. Dacthal®:

   * Diamond Shamrock Chemical Company; Greens Bayou, Texas.

If substantial HCB and HCBD contamination is shown to result from operation of the chlorine plants previously listed, monitoring should also be undertaken at:

* Champion International Corporation; Houston, Texas (diaphragm cell).

* Linden Chlorine Products, Inc.; Linden, New Jersey (mercury cell).

It is also recommended that samples of mirex and hexachlorocyclopentadiene be obtained and analyzed. If product contamination by HCB or HCBD is demonstrated, monitoring should be undertaken at the Occidental Petroleum Company's Niagara Falls plant.

IV. DISCUSSION OF METHODOLOGY

A series of studies was conducted to develop information on the potential hazards to man associated with the production and use of a class of chemicals related to hexachlorobenzene and hexachlorobutadiene. A discussion of each major phase of the methodology employed in Task I follows.

A. Selection of Toxic Substances

At the beginning of the program, the EPA task officer designated five chemical substances as subjects for the Task I investigations. As the study developed MRI determined, through discussions with industry spokesmen and a survey of technical literature on the chemical process industry, that production of several additional substances was a potential source for escape of HCB and/or HCBD into the environment. During consultations with the EPA task officer, it was mutually agreed that 18 additional substances would also be investigated. These 18 substances were included because it was established that their production posed either a proven or a potential source of HCB and/or HCBD formation.

B. Identification of Production Sites and Estimated Production Volumes

1. Production sites: The domestic production sites for each substance were identified, using several standard reference publications, including the following:

* Stanford Research Institute, Directory of Chemical Producers, Chemical Information Services, Menlo Park, California (1973 and 1974).

* Stanford Research Institute, Chemical Economics Handbook, Chemical Information Services, Menlo Park, California (1973 and 1974).

* Buyers Guide, Chemical Week (1973 and 1974).

* Manufacturing Chemists Association, Inc., Chemical Statistics Handbook, 7th ed. (1971).

* U.S. Tariff Commission, Synthetic Organic Chemicals: U.S. Production and Sales, T.C. Publication No. 479, U.S. Government Printing Office, Washington, D.C. (1972).

The last publication listed was particularly helpful in distinguishing producers from other sources. In some cases, telephone contacts were made to confirm information derived from the various references.

The names of the producers of each selected substance and the geographic location of each production site in the United States were tabulated. For all chemicals of special interest, maps were prepared showing the geographical distribution of the production facilities and the corresponding EPA regions. These maps are included with the discussions in the next section of the report.

2. Production capacity, production volumes, and imports: Some problems were encountered in collecting the required data on production capacities, production volumes, and projected production volumes by the major producers of each chemical. Most of the standard reference publications do not list production data for some chemicals of interest to the project (e.g., hexachlorobenzene, hexachloroethane and pentachlorobenzene) which are either produced in very small quantities or as captive intermediate chemicals or by-products. Several company spokesmen declined to respond to telephone inquiries on this subject; they replied that such information was proprietary. Telephone and letter inquiries, made to chemical trade organizations and chemical distributors, provided additional data on production capacities and production volumes.

Information concerning imports was obtained from technical literature and the Kansas City, Missouri, Office of the U.S. Department of Commerce.

V. PRODUCTION SITES AND VOLUMES

This section provides a brief synopsis of plant locations and production volumes for each of the 23 chemicals studied. Complete lists of individual plant sites and production volumes, together with annual gross production and import figures for as many years as are available, are appended to this report (Appendix A). Maps showing the plant locations appear in this section, immediately after discussion of the substance(s) shown. All production quantities are given in short tons for 1972, and the data for number of production sites and number of manufacturers applies for 1973, except as otherwise noted.

Table I presents a summary of the number of domestic production sites and manufacturers, and the production volumes for each of the chemicals investigated. Individual discussions for each chemical are given in the following subsections.

A. Hexachlorobenzene (HCB, C_6Cl_6)

As shown in Figure 1, there were three production sites (Dover Chemical Company, Dover Ohio; Hummel Chemical Company, South Plainfield, New Jersey; and Stauffer Chemical Company, Louisville, Kentucky) operating through 1973. In 1974, the Dover and Hummel plants were reported to have been shut down, leaving Stauffer as the only domestic producer. The estimated total production in 1973 was 350 tons. Efforts to obtain information on whether Hummel and Dover have been repackaging or marketing HCB were unsuccessful.

B. Hexachlorobutadiene (HCBD, $CCl_2=CCl-CCl=CCl_2$)

Hexachlorobutadiene has not been produced in the U.S. since 1970, because of poor domestic demand. Prior to that time, HCBD was produced domestically as a recovered by-product in the manufacture of perchloroethylene and trichloroethylene. The technical literature indicates that three HCBD production sites were used prior to 1970 (see Figure 1). In 1974, all commercial quantities (200,000 to 500,000 lb) of HCBD, sold in the U.S., were imported by Dynamit Nobel America from Germany.[2]

C. Chlorine (Cl_2)

There are approximately 70 chlorine production sites and 32 manufacturing companies. As shown in Figure 2, these sites are concentrated in the eastern one-third of the U.S., and along the coastlines. In addition to chlorine, most of these sites also product coproducts, such as caustic soda, caustic potash, soda ash, sodium metal, and magnesium. Louisiana and Texas have the largest number of production sites (nine in Louisiana and 10 in Texas).

TABLE I

SUMMARY OF NUMBER OF DOMESTIC PRODUCTION SITES AND MANUFACTURERS AND THE PRODUCTION VOLUMES FOR SELECTED CHEMICALS

Item	Chemical	No. of Active Production Sites[a]	No. of Manufac-turers[a]	Production Volume (short tons)[b]
A	Hexachlorobenzene	3	3	350[d]
B	Hexachlorobutadiene	0	0	0
C	Chlorine	70[c]	32	9,868,000
	Sodium Metal	5	3	75[e]
D	Sodium Chlorate	15	10	214,000
E	Carbon Tetrachloride	11	6	498,500
F	Perchloroethylene	10	7	367,000
G	Trichloroethylene	5	5	213,500
H	Vinyl Chloride Monomer	16	12	2,544,500
I	Hexachloroethane	1	1	200
J	Pentachlorobenzene	6	6	< 1[f]
K	Pentachlorophenol	4	4	24,500
L	Synthetic Rubber (Chloroprene)	6	4	178,000[e]
M	Atrazine	2	1	50,000
	Propazine	1	1	2,000
	Simazine	1	1	4,000
N	Pentachloronitrobenzene	2	1	1,500
O	Dacthal®	1	1	1,000
P	Mirex	1	1	< 500
Q	Maleic Hydrazide	4	4	4,000
R	Hexachlorocyclopentadiene	4	2	25,000
S	Chlorinated Naphthalenes	1	1	< 2,500
T	Chlorinated Biphenyls	1	1	19,300

---

a/ Applies for 1973.

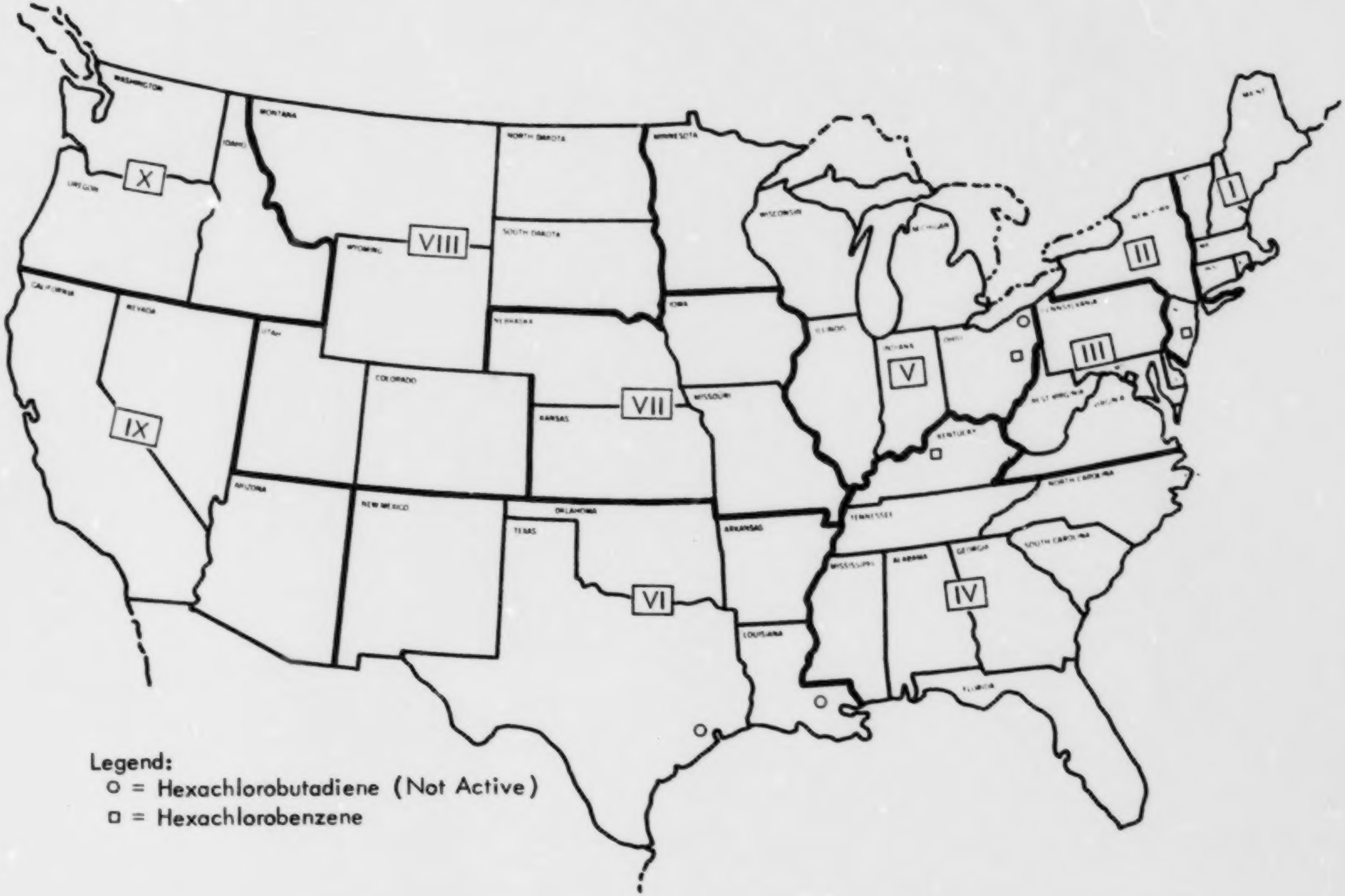
b/ Applies for 1972, except where otherwise noted.

c/ Includes 5 sodium production sites at which chlorine is produced as by-product.

d/ Applies for 1973.

e/ Applies for 1971.

f/ MRI estimate of domestic production in 1972 for commercial sales. See Appendix A (p. 126) for basis of estimate.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MISSOURI
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VIRGINIA
KENTUCKY
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ARIZONA
NEW MEXICO
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TEXAS
ARKANSAS
MISSISSIPPI
ALABAMA
GEORGIA
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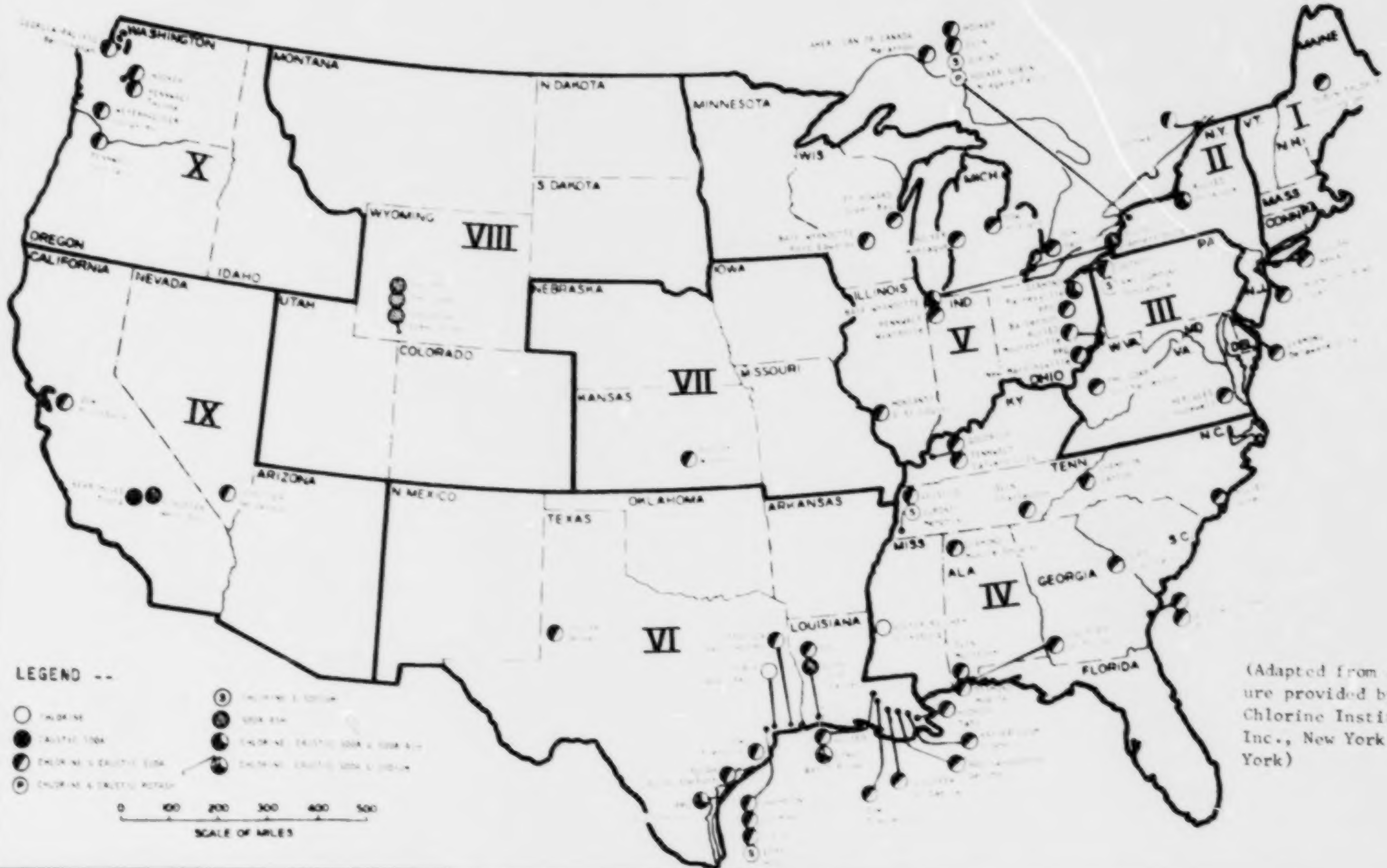
Legend:
○ = Hexachlorobutadiene (Not Active)
□ = Hexachlorobenzene

Figure 1 - Production Sites for Hexachlorobenzene and Hexachlorobutadiene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ALA
GEORGIA
FLORIDA
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LEGEND --
CHLORINE
CAUSTIC SODA
CHLORINE & CAUSTIC SODA
CHLORINE & CAUSTIC POTASH
CHLORINE & SODIUM
SODA ASH
CHLORINE, CAUSTIC SODA & SODA ASH
CHLORINE, CAUSTIC SODA & SODIUM
0
100
200
300
400
500
SCALE OF MILES

(Adapted from a figure provided by the Chlorine Institute, Inc., New York, New York)

Figure 2 - Operating Chlorine and Alkali Plants in the United States and Canada (January 1, 1974)

Total chlorine production was about 9,868,000 tons in 1972. Individual reported plant production capacities range from 14,000 (Houston, Texas) to 1,700,000 (Freeport, Texas) tons/year. Some production figures were reported as a consolidated number for several plants; some plants' capacities could not be determined.

Sodium metal production plants are included in this category, since chlorine is a by-product. The reported individual production capacities for the five sodium plants range from 15 to 23 tons/year. Total production of sodium in 1972 was only 75 tons.

D. Sodium Chlorate ($NaClO_3$)

There are 10 manufacturers and 15 production sites for sodium chlorate. Nine sites are located in southern states as shown in Figure 3. An estimated total production for 1972 was 214,000 tons. The largest plant capacity (Columbus, Mississippi) is 62,000 tons/year; the smallest capacity (Bellingham, Washington, and Butler, Alabama) is 4,000 tons/year.

E. Carbon Tetrachloride (CCl_4)

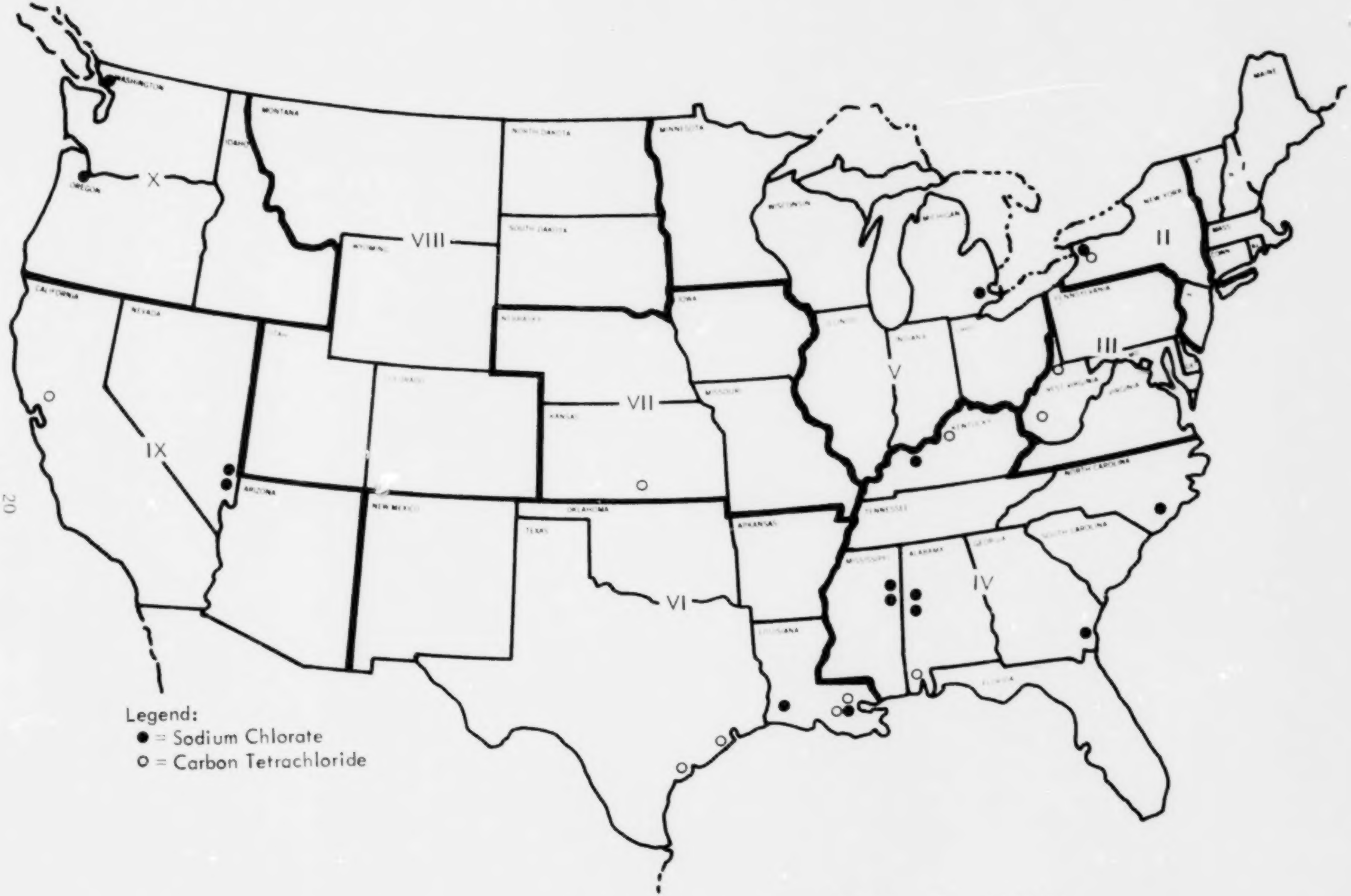
There are 11 production sites and six manufacturers of this chemical. Figure 3 shows that five sites are located in southern states (Texas - 2, Louisiana - 2, and Alabama - 1). Total production in 1972 was about 498,500 tons. The reported plant capacities range from 4,000 (Moundsville, West Virginia) to 250,000 (Corpus Christi, Texas) tons/year.

F. Perchloroethylene (C_2Cl_4)

The seven producers and 10 production sites accounted for a total production of about 367,000 tons of perchloroethylene in 1972. As indicated in Figure 4, seven of the 10 plant sites are located in Louisiana and Texas. Plant production capacities extend from a low of 10,000 (Pittsburg, California) to a high of 100,000 (Lake Charles, Louisiana) tons/year.

G. Trichloroethylene (C_2HCl_3)

This chemical is produced by five manufacturers and there are five production sites. Figure 4 shows that Louisiana has three sites and Texas has two. The total production of trichloroethylene in 1972 was about 213,500 tons. Individual plant capacities are reported to range from 20,000 (Taft, Louisiana) to 140,000 (Lake Charles, Louisiana) tons/year.


Legend:
● = Sodium Chlorate
○ = Carbon Tetrachloride
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NORTH DAKOTA
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MICHIGAN
ILLINOIS
INDIANA
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TENNESSEE
MISSISSIPPI
ALABAMA
GEORGIA
FLORIDA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
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MASS
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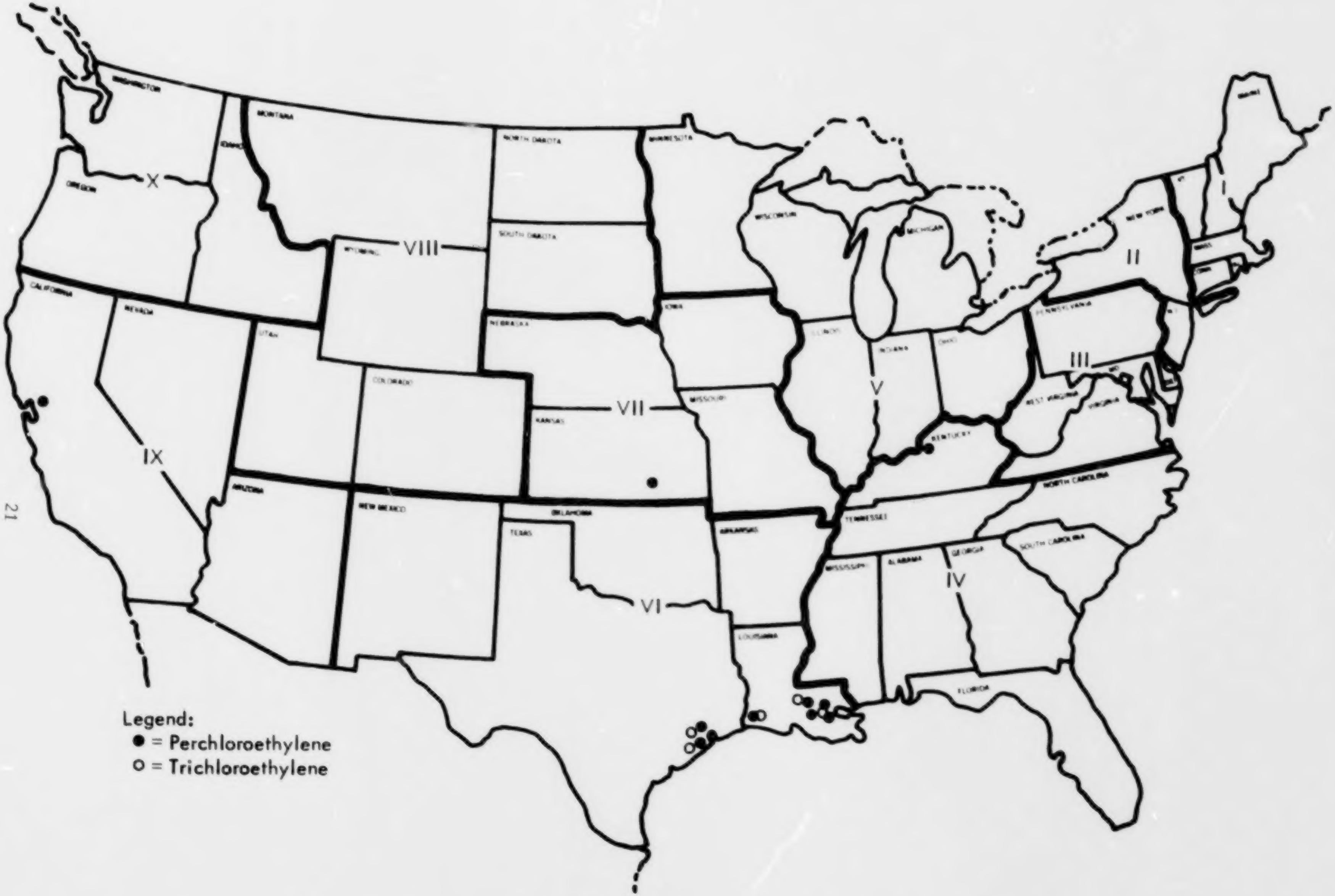
Figure 3 - Production Sites for Sodium Chlorate and Carbon Tetrachloride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Legend:
● = Perchloroethylene
○ = Trichloroethylene

Figure 4 - Production Sites for Perchloroethylene and Trichloroethylene

H. Vinyl Chloride Monomer (CH_2=CHCl)

Thirteen of the 16 production sites are located in Louisiana and Texas (see Figure 5); there are 12 manufacturing companies. Total production of vinyl chloride monomer amounted to about 2,544,500 tons in 1972. The reported individual plant capacities range from 75,000 (Pasadena, and Texas City, Texas) to 500,000 (Calvert, City, Kentucky) tons/year.

I. Hexachloroethane (C_2Cl_6)

Hexachloroethane is produced at only one site (see Figure 5). Total production in 1972 was about 200 tons. Production capacity of the Hummel plant in South Plainfield, New Jersey, is estimated to be 250 tons/year.

J. Pentachlorobenzene (C_6HCl_5)

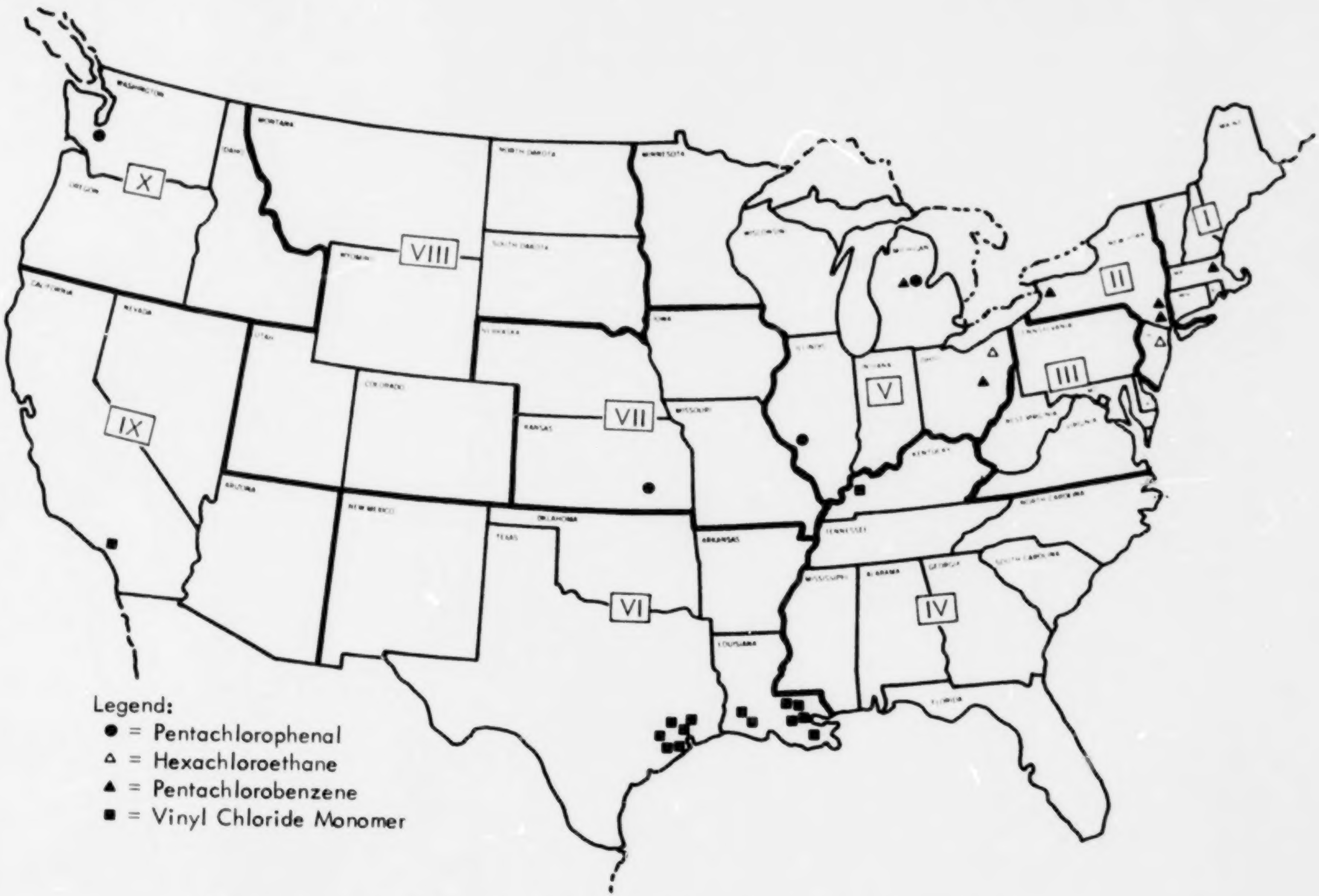
In addition to captive production as a by-product by four companies, this chemical is also produced in small quantities by two specialty chemical companies in the New York City Area (see Figure 5). The estimated domestic production for commercial sales in 1972 is less than 1 ton. Data on individual plant capacities for captive production could not be obtained.

K. Pentachlorophenol (PCP, C_6Cl_5OH)

Four companies manufacture this chemical; and there are four production sites (see Figure 5). Total production was about 24,500 tons in 1972. The individual plant production capacities are reported to range from about 3,500 (Wichita, Kansas) to 13,000 (Sauget, Illinois) tons/year.

L. Synthetic Rubber (Chloroprene, CH_2=CH-CCl=CH_2)

Since chloroprene appears to represent the only type of synthetic rubber production which has potential for production of HCB and HCBD, this was the only rubber process investigated. There are six manufacturing sites (see Figure 6), and four producers for chloroprene. The estimated total production for 1971 is 178,000 tons. Three of these plant sites have capacities ranging from 22,500 (Houston, Texas) to 137,500 (Louisville, Kentucky) tons/year. The total production capacity reported by the industry for 1971 was 198,000 tons.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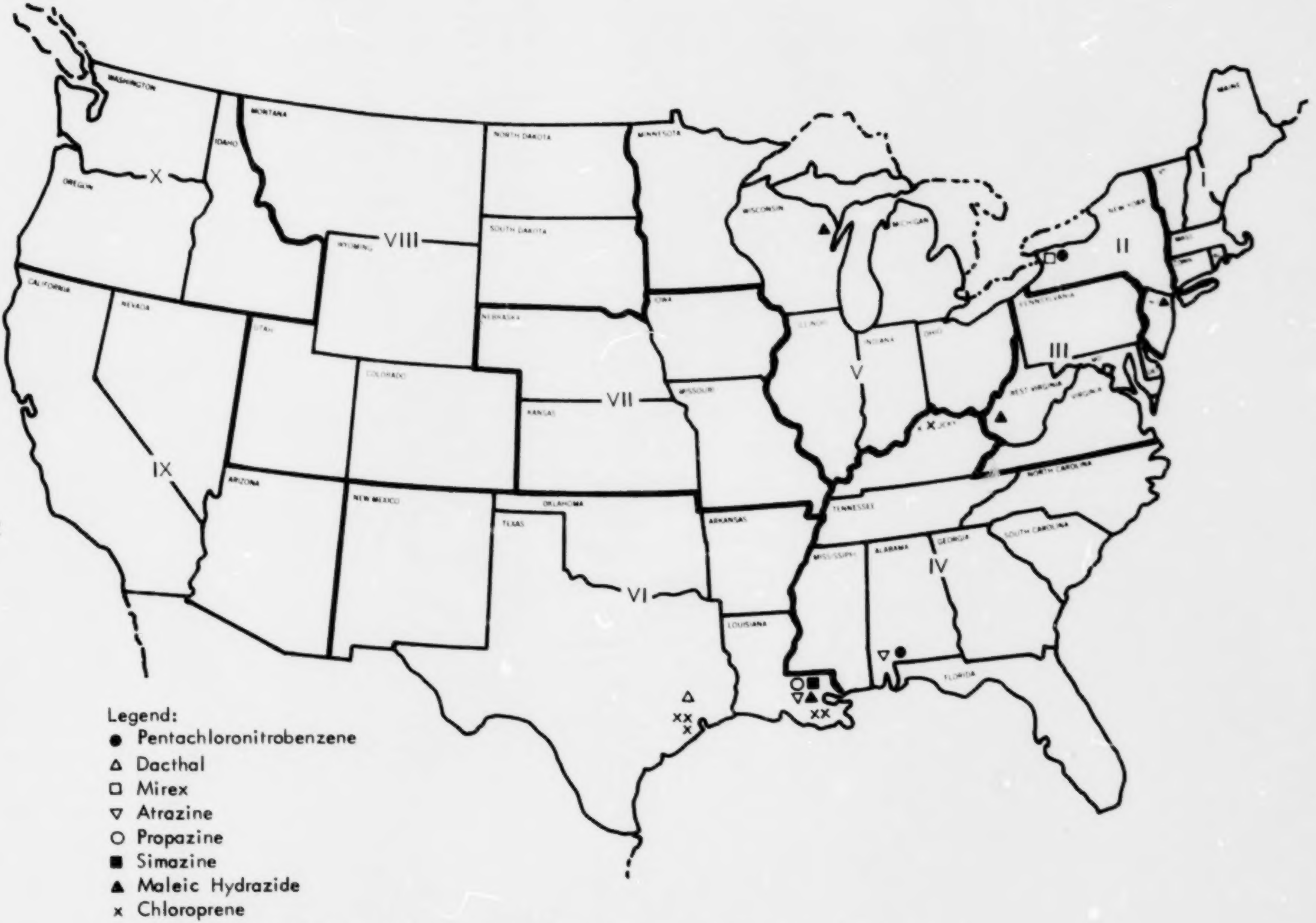
Legend:
● = Pentachlorophenal
△ = Hexachloroethane
▲ = Pentachlorobenzene
■ = Vinyl Chloride Monomer

Figure 5 - Production Sites for Pentachlorophenol, Hexachloroethane, Pentachlorobenzene, and Vinyl Chloride Monomer


Legend:
● Pentachloronitrobenzene
△ Dacthal
□ Mirex
▽ Atrazine
○ Propazine
■ Simazine
▲ Maleic Hydrazide
× Chloroprene
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WEST VIRGINIA
PENNSYLVANIA
NEW YORK
MAINE

Figure 6 - Production Sites for Pentachloronitrobenzene, Dacthal, Mirex, Atrazine, Propazine, Simazine, Maleic Hydrazide and Synthetic Rubber (Chloroprene)

M. Atrazine, Propazine, and Simazine

These chemicals are members of a family of triazine compounds $[C_3N_3Cl(NHR)_2]$ used in herbicide applications. They are now produced solely by the Ciba-Geigy Corporation at St. Gabriel, Louisiana; atrazine was also produced by the same company at McIntosh, Alabama in 1973 (see Figure 6). In 1972, the estimated production volumes for atrazine, propazine, and simazine were 50,000, 2,000, and 4,000 tons, respectively. The McIntosh, Alabama, facility is reported to have a production capacity of over 75,000 tons/year; data on capacities for other sites could not be ascertained.

N. Pentachloronitrobenzene (PCNB, $C_6Cl_5 \cdot NO_2$)

There are two production facilities and one manufacturer for this product (see Figure 6). The estimated total production in 1972 was 1,500 tons, and the estimated production capacity for the same year was 2,000 tons.

O. Dacthal $[C_6Cl_4(COOCH_3)_2]$

As shown in Figure 6, this pesticide is produced at one plant site (Greens Bayou, Texas); the production volume in 1972 was about 1,000 tons. The estimated production capacity for the same year was 1,300 tons.

P. Mirex ($C_{10}Cl_{12}$)

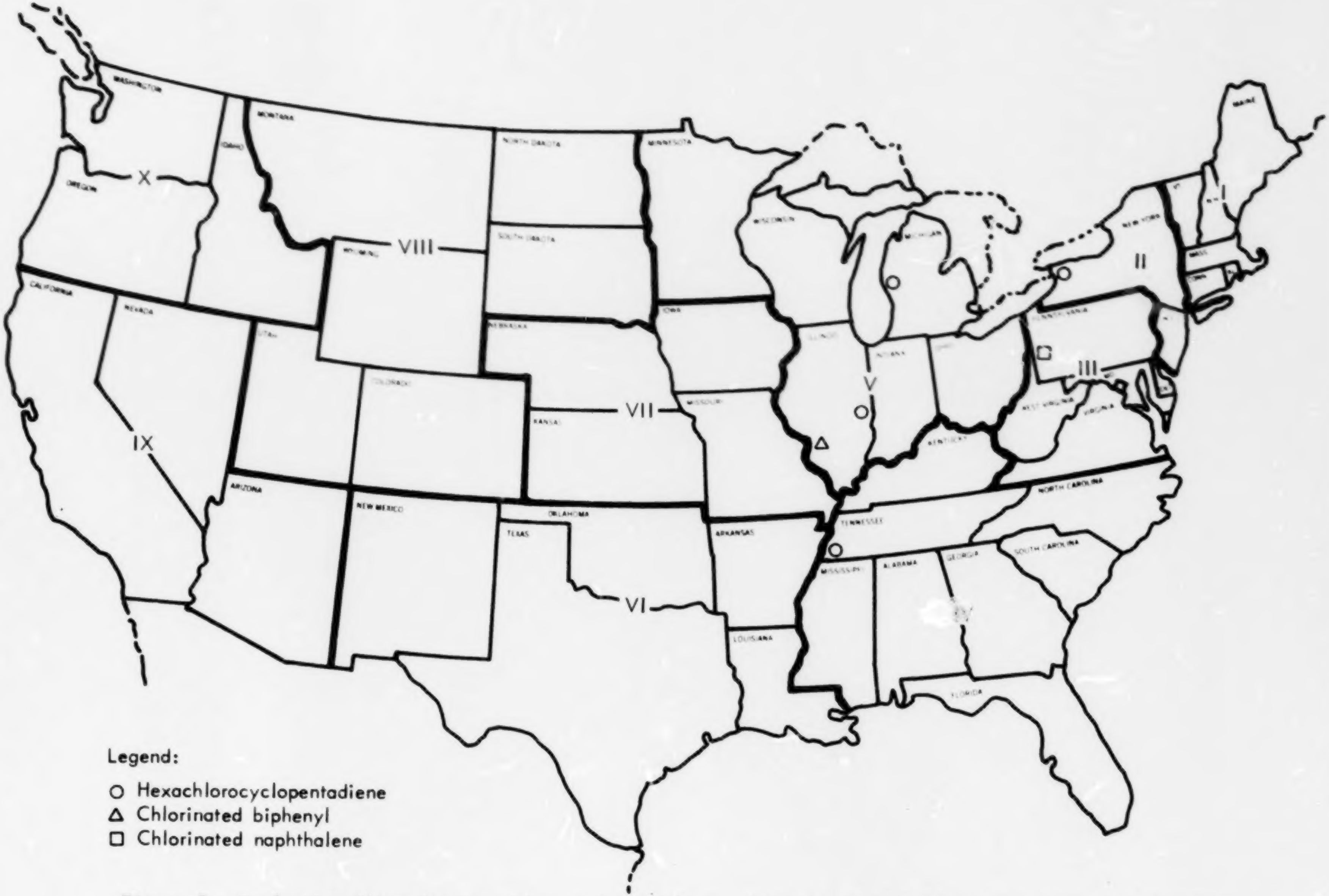
Mirex was produced at only one plant site in 1973 (see Figure 6). Two plants were in operation in 1972, and they had a combined annual production of less than 500 tons. The total capacity was estimated to be less than 600 tons/year.

Q. Maleic Hydrazide (NH-CO-CH=CH-CO-NH)

There are four production sites and four manufacturers for this product (Figure 6). Total production in 1972 amounted to about 4,000 tons and the plant capacity was estimated at 5,000 tons.

R. Hexachlorocyclopentadiene (HCP, C_5Cl_6)

The locations of the four manufacturing plants for HCP are shown in Figure 7; there are two manufacturers. The estimated total HCP volume for all domestic producers in 1972 is 25,000 tons. Total plant capacity for the same year was estimated to be 30,000 tons.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MISSISSIPPI
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GEORGIA
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Legend:
○ Hexachlorocyclopentadiene
△ Chlorinated biphenyl
□ Chlorinated naphthalene

Figure 7 - Production Sites for Hexachlorocyclopentadiene, Chlorinated Biphenyls and Chlorinated Naphthalenes

S. Chlorinated Naphthalenes ($C_{10}H_{8-x}Cl_x$)

The only domestic producer is the Koppers Company, which operates a production facility at only one site (see Figure 7). The sales volume for all of these products from 1969 to 1974 has averaged less than 2,500 tons/year. Total plant capacity is estimated to be 3,000 tons/year.

T. Chlorinated Biphenyls ($C_{12}H_{10-x}Cl_x$)

Monsanto Company, the sole producer, operates only one production facility (see Figure 7). In April 1971, Monsanto closed its Anniston, Alabama production plant for PCBs. The total domestic production of PCBs in 1972 was 19,300 tons, and the estimated total capacity was 24,000 tons.

VI. MANUFACTURING METHODS, BY-PRODUCTS, CONTAMINATION, AND RISKS

The following discussions cover the basic process technology for each of the 23 chemicals, with particular emphasis on the existing and potential sources of HCB and HCBD. This section also discusses, in a general manner, the operating parameters that affect the production of these chemicals as by-products or wastes. Some of the information in this section was obtained from questionnaires (see Appendix B).

The chemical production processes described in this section are divided into two subsections.

A. Processes known to produce HCB and/or HCBD, and

B. Processes with theoretical, but not proven, production of HCB and/or HCBD.

Following the discussion of Type A and B processes, a subsection (C) is presented which covers the methodology and results of a study conducted to estimate the quantities of HCB and/or HCBD contained in domestic processing wastes, by-products, and products.

A. Processes Known to Produce HCB and/or HCBD

1. Hexachlorobenzene (HCB): Domestic producers of HCB have indicated that manufacturing methods for this chemical are proprietary, and, therefore, only a limited amount of information was obtained from processors concerning the current production operations.

Representatives of the Stauffer Chemical Company have indicated that at their Louisville, Kentucky, plant HCB is a by-product in the manufacture of perchloroethylene. The HCB is recovered from a by-product tar, which contains 80% HCB and 10% HCBD, and the remainder of the tar is reported to be recycled to the process. Under these operating conditions, the possibility of HCB or HCBD entering the environment is considered to be slight.

There are two basic processes described in the technical literature[4,6] which could be used to produce HCB directly: (a) treatment of isomers of hexachlorocyclohexane ($C_6H_6Cl_6$) with sufuryl chloride (SO_2Cl_2) and (b) reacting benzene (C_6H_6) or chlorobenzenes with chlorine. These basic processes are discussed in the following subsections.

a. Production of hexachlorobenzene from hexachlorocyclohexane[4,6]

(1) Process flow diagram: A schematic production flow diagram is shown in Figure 8.

(2) Process description: Hexachlorobenzene (HCB, formula C_6Cl_6) may be produced by refluxing isomers of hexachlorocyclohexane (formula $C_6H_6Cl_6$) with sulfuryl chloride (SO_2Cl_2) or chlorosulfonic acid ($HClSO_3$) in the presence of ferric chloride ($FeCl_3$) or aluminum chloride ($AlCl_3$) as catalyst, at 130 to 200°C. Refluxing is continued for several hours. The HCB, which crystallizes when the reaction medium is cooled, is removed by filtration or centrifugation, and washed with water.

(3) Reaction:

$$\text{Hexachlorocyclohexane} + \text{Chlorosulfonic Acid} \longrightarrow \text{HCB} + \text{Hydrogen Chloride} + \text{Sulfurous Acid}$$

(4) Raw materials:

Hexachlorocyclohexane isomers, normally from gamma-hexachlorocyclohexane production (lindane)

Sulfuryl chloride or chlorosulfonic acid

Ferric chloride or aluminum chloride

(5) Resource requirements:

Water

(6) By-products and wastes:

Hydrogen chloride

Sulfurous acid (decomposes to H_2O and SO_2)

b. Production of HCB from benzene and chlorobenzenes[4,6]

(1) Process flow diagram: A schematic production flow diagram is shown in Figure 9.

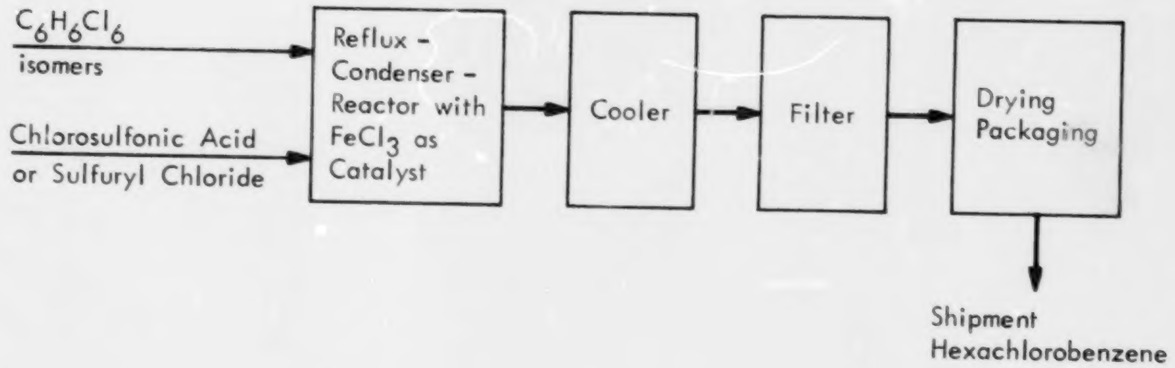

$C_6H_6Cl_6$ isomers
Chlorosulfonic Acid or Sulfuryl Chloride
Reflux - Condenser - Reactor with $FeCl_3$ as Catalyst
Cooler
Filter
Drying Packaging
Shipment Hexachlorobenzene

Figure 8 - Production Schematic for Hexachlorobenzene from Hexachlorocyclohexane[4,6]

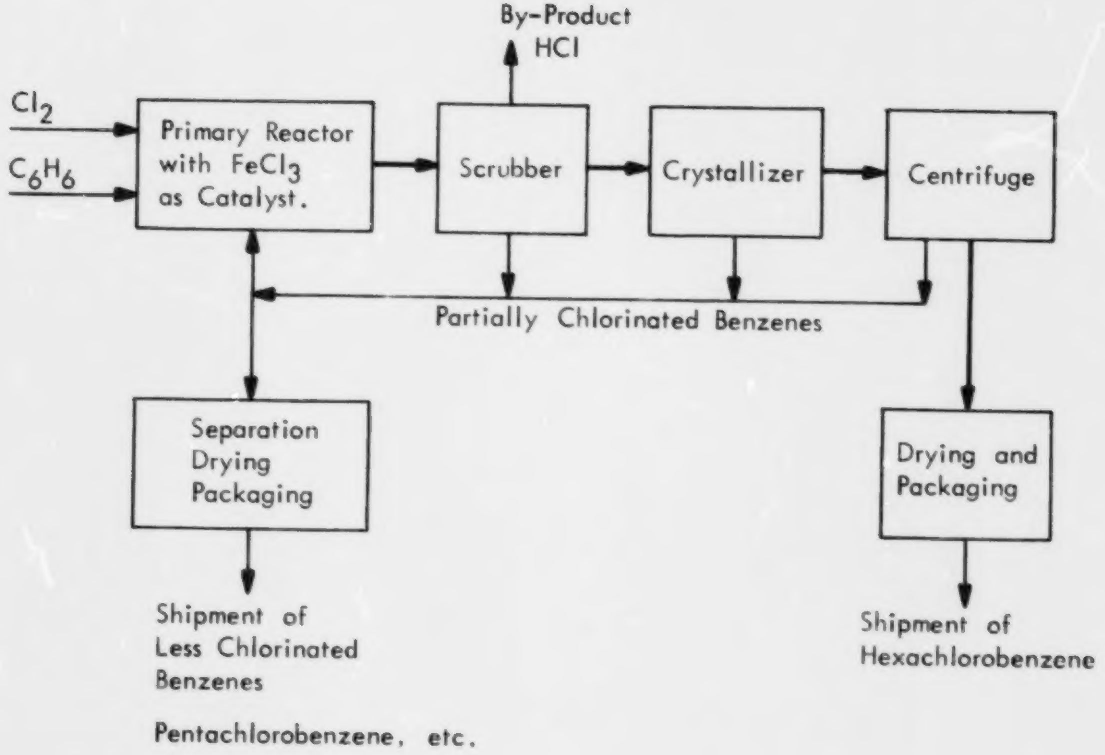

By-Product
HCl
Cl_2
C_6H_6
Primary Reactor with $FeCl_3$ as Catalyst.
Scrubber
Crystallizer
Centrifuge
Partially Chlorinated Benzenes
Separation
Drying
Packaging
Drying and Packaging
Shipment of Less Chlorinated Benzenes
Pentachlorobenzene, etc.
Shipment of Hexachlorobenzene

Figure 9 - Production Schematic for Hexachlorobenzene by Chlorination of Benzene and Chlorobenzenes[4,6]

(2) Process description: Hexachlorobenzene may be produced by reacting benzene (C_6H_6) with excess chlorine (Cl_2) in the presence of ferric chloride ($FeCl_3$) catalyst at 150 to 200°C. The reaction products are scrubbed with water to remove hydrogen chloride (HCl). Gaseous chlorobenzenes are reçycled from the scrubber to the initial reactor. The scrubber reaction products are then cooled to 100°C, allowing HCB to crystallize and precipitate from any liquid chlorobenzenes. Solid HCB is removed by centrifuge and dried. Liquid chlorobenzenes passing through the centrifuge are recycled to the primary reactor.

(3) Reaction:

$$C_6H_6 + 6Cl_2 \xrightarrow[150\text{-}200^\circ C]{FeCl_2} C_6Cl_6 + 6HCl$$

(4) Raw materials:

Benzene or chlorobenzenes

Chlorine

Ferric chloride (catalyst)

(5) Resource requirements:

Water

(6) By-products and wastes:

Pentachlorobenzene

Partially chlorinated benzenes

Hydrogen chloride

2. Hexachlorobutadiene: Hexachlorobutadiene is not currently produced in the U.S. Domestic production (solely as by-product) was terminated about 1970 because of unattractive production and marketing conditions. In 1974, all commercial quantities of HCBD (200,000 to 500,000 lb/year) were being imported from Dynamit Nobel in Germany.[2] HCBD was formerly produced as a recovered by-product in the production of perchloroethylene.

Descriptions of processes for perchloroethylene in which HCBD can be produced as a recovered by-product are presented in this section beginning on page 40.

A patented process (U.S. Patent 2,269,600, January 1942) for direct synthesis of HCBD involves the chlorination and dehydrochlorination of hexachlorobutene. An experimental method for preparation of HCBD by chlorination of polychlorobutanes (at 425 to 500°C) is described in the technical literature.[7] No evidence was found that either of these processes have ever been used commercially in the U.S.

3. Chlorine:[4] Chlorine (Cl_2) is produced by electrolysis of purified and concentrated sodium chloride (NaCl) brine. Two types of electrolysis cells are used: the diaphragm cell and the mercury cell. A description of each process follows under separate headings.

a. Chlorine manufacture in diaphragm cells

(1) Process flow diagram: A schematic production flow diagram is shown in Figure 10.

(2) Process description:[4] Chlorine (Cl_2) may be produced by electrolysis of sodium chloride (NaCl) brine. The process begins with obtaining, concentrating, and purifying a brine. The brine is then passed into the diaphragm cell where Cl_2 gas is evolved from the anode. Previously, almost all anodes were made of graphite, but recently metal oxide anodes (called dimensionally stabilized anodes, DSA) have been introduced. The electrolysis produces hydrogen (H_2) gas at the cathode, rather than metallic sodium, and a caustic soda (NaOH) solution is formed. The diaphragm serves to separate the anodic and cathodic solutions and evolved gases. The spent brine proceeds to a concentration unit and the caustic is recovered. The Cl_2 and H_2 are purified and dried for packaging.

(3) Reaction:

$$2\ NaCl + 2H_2O \xrightarrow{\text{electrolysis}} Cl_2 + H_2 + 2\ NaOH$$

(4) Raw materials:

Sodium chloride

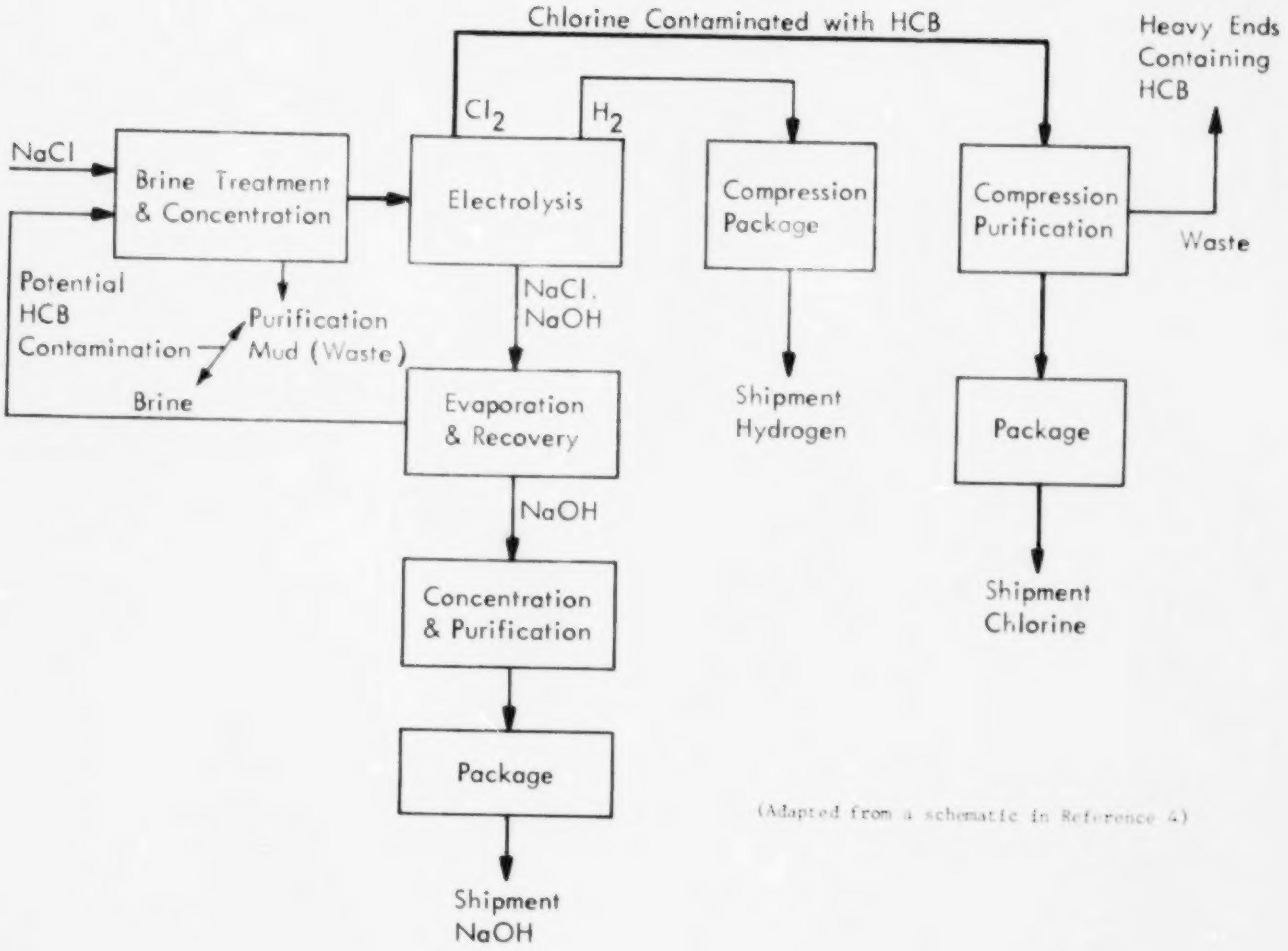
(5) Resource requirements:

Sodium chloride

Water

(6) Energy requirements:

Electricity, 2,700 kw-hr/ton Cl_2


Chlorine Contaminated with HCB
Heavy Ends Containing HCB
NaCl
Brine Treatment & Concentration
Electrolysis
Cl_2
H_2
Compression Package
Compression Purification
Waste
Potential HCB Contamination
Purification Mud (Waste)
Brine
NaCl. NaOH
Evaporation & Recovery
Shipment Hydrogen
Package
NaOH
Concentration & Purification
Shipment Chlorine
Package
Shipment NaOH

(Adapted from a schematic in Reference 4)

Figure 10 - Production Schematic for Chlorine in Diaphragm Cells

(7) By-products and wastes:

Hydrogen

Caustic soda

Processes using graphite anodes have potential for production of by-product hexachlorobenzene. Plants that have converted from graphite anodes to metal oxide anodes (DSA) no longer have a problem with HCB formation.

b. Chlorine production in mercury cells

(1) Process flow diagram: A schematic production flow diagram is shown in Figure 11.

(2) Process description:[4] Chlorine (Cl_2) may be produced by electrolysis of sodium chloride (NaCl) brine in mercury cells. Brine is concentrated and purified and passed into the electrolytic cell where Cl_2 is evolved from the anode, which is usually graphite. The cathode in a mercury cell is a flowing sheet of liquid mercury (Hg). The sodium forms an amalgam with the mercury [Na(Hg)] and is continuously carried into the amalgam decomposer. Normally the amalgam is then intimately contacted with water to form caustic soda (NaOH) and hydrogen (H_2) gas. The mercury regenerated is recycled to the cathode. Alternatively, the sodium can be recovered as the metal, if preferred.

(3) Reaction:

$$2\ NaCl + 2\ Hg \xrightarrow{\text{electrolysis}} Cl_2 + 2\ Na(Hg)$$

$$2\ Na(Hg) + 2\ H_2O \longrightarrow 2\ NaOH + H_2 + 2\ Hg$$

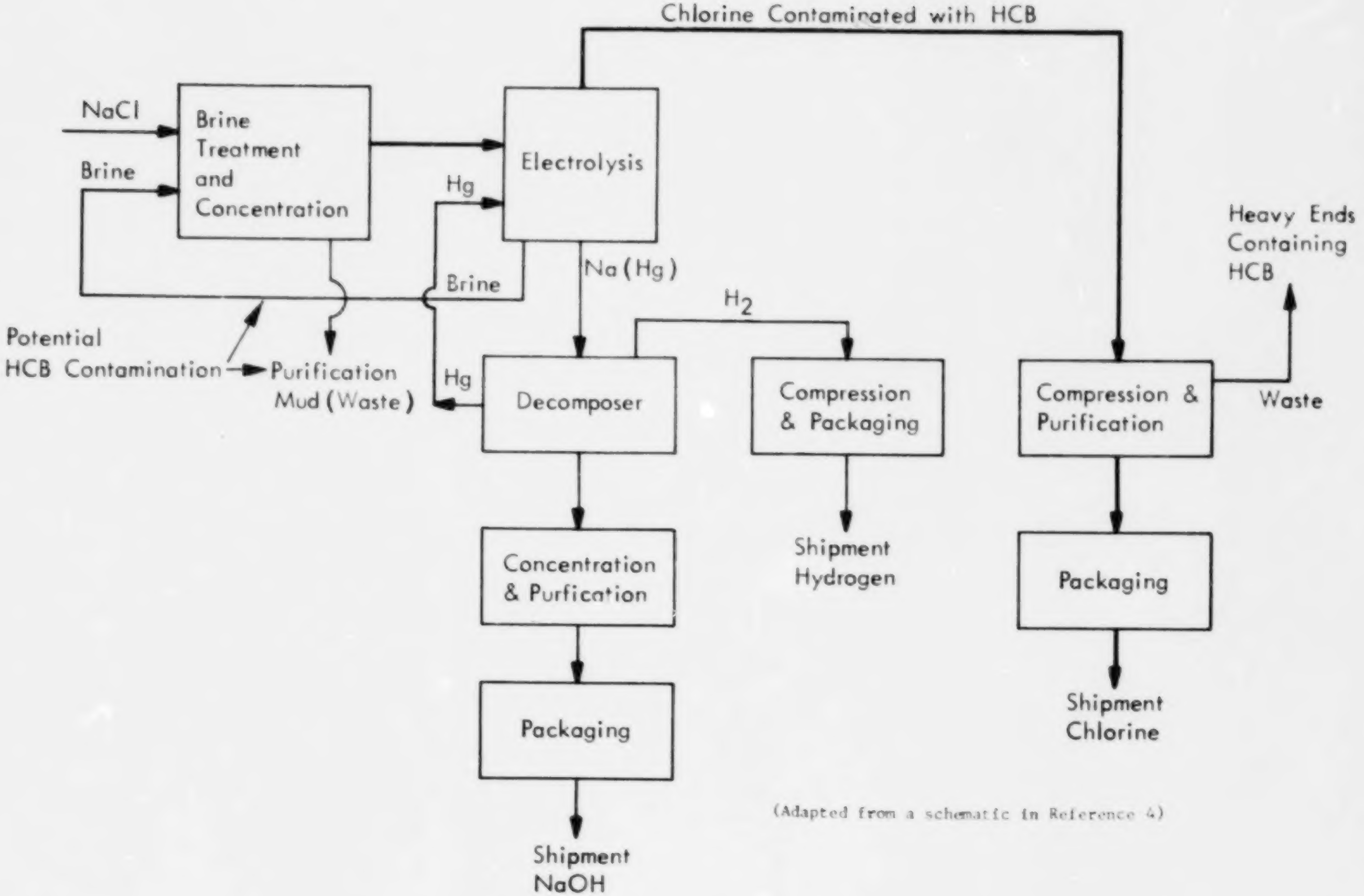
(4) Raw materials:

Sodium chloride

(5) Resource requirements:

Sodium chloride

Water


Chlorine Contaminated with HCB
NaCl
Brine
Brine Treatment and Concentration
Electrolysis
Hg
Brine
Na (Hg)
H_2
Heavy Ends Containing HCB
Potential HCB Contamination
Purification Mud (Waste)
Hg
Decomposer
Compression & Packaging
Compression & Purification
Waste
Concentration & Purfication
Shipment Hydrogen
Packaging
Packaging
Shipment Chlorine
Shipment NaOH

(Adapted from a schematic in Reference 4)

Figure 11 - Production Schematic for Chlorine in Mercury Cells

(6) Energy requirements:

Electricity - 3,200 kw-hr/ton Cl_2

(7) By-products and wastes:

Hydrogen

Caustic soda

Processes using graphite anodes have potential for production of by-product hexachlorobenzene and hexachlorobutadiene. Some plants have converted from graphite anodes to metal oxide anodes (DSA) and no longer have a problem with HCB formation.

The process wastes from these electrolytic processes (either diaphragm or mercury cell) have a significant potential for the formation of HCB and other hydrocarbon waste materials in the crude Cl_2 gas when graphite anodes are used, as was previously the worldwide practice. In both processes, crude Cl_2 gas is liquified and then purified by a distillation step, so that most of the chlorinated hydrocarbons are separated from the Cl_2 and remain as components of the "heavy ends" from the distillation step. A minor potential exists for HCB contamination of the recycled, spent brine, and of the brine purification mud: the technical literature indicates this is not a significant problem.[8]

Industry spokesmen state that the substitution of a metallized anode (DSA for dimensionally stable anode) for the graphite anode in either process completely eliminates the HCB problems. Since about 1969, many plants have been converted to the use of the DSAs. The DSAs offer a substantial reduction in the consumption of electricity and in maintenance requirements when used in the chlorine industry.

The typical chlorinated hydrocarbon wastes from the Cl_2 liquefication and purification steps of the diaphragm process range from 0.70 to 1.4 lb/ton of chlorine product.

The typical raw waste loads (based on 21 facilities) from the mercury cell process[8] are shown in Table II.

4. Carbon tetrachloride: The most important domestic production route is the chlorination of hydrocarbons, particularly methane.[4] About 60% of the total production is accomplished by this method. About 40% of the production involves a low temperature reaction between carbon disulfide and chlorine. A discussion of these production methods is given in the following subsections.

TABLE II

RAW WASTE LOADS FROM MERCURY CELL PROCESS[a]

	Waste Load (lb/ton Cl_2 product) Mean	Range
Purification muds, $CaCO_3$ and $Mg(OH)_2$	33	1.0-70
NaOH	27	1.0-64
NaCl	422	30-1,000
KCl	0	-
H_2SO_4	32	0-100
Chlorinated Hydrocarbons[a]	1.4	0-3.0
Na_2SO_4	31	0-126
Cl_2 (as $CaOCl_2$)	22	0-150
Filter aids	1.70	0-10
Mercury	0.30	0.04-0.56
Carbon, graphite	40.6	0.70-680

---

[a] Depends markedly on grade of chlorine produced (i.e., degree of purification).

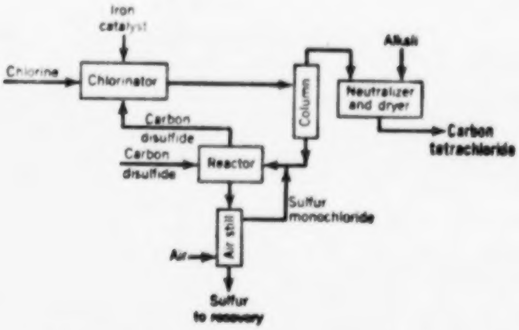
a. Production by chlorination of hydrocarbons:[4] The chlorination of aliphatic or aromatic hydrocarbons at pyrolytic temperatures generally results in production of some carbon tetrachloride, along with other chloromethanes and higher chlorination derivatives. Chlorination at such temperatures is often referred to as chlorinolysis, since it involves a simultaneous breakdown of the hydrocarbons and chlorination of the molecular fragments. This type of chlorination is highly favorable to the formation of by-product HCB and HCBD. The quantity of carbon tetrachloride produced depends on the nature of the hydrocarbon starting material and the conditions of chlorination. When the hydrocarbon is methane, conditions can be set to obtain yields greater than 70% carbon tetrachloride.

In the Huls process, a 5:1 mixture (by volume) of chlorine and methane is reacted at 650°C; this temperature is maintained by control of the gas flow rate. The exit gas is cooled at 450°C and then passed to a second reactor where more methane is added to the gas stream. The principal by-product is perchloroethylene. When ethylene is substituted for methane in this process, perchloroethylene becomes the main product and carbon tetrachloride is one of a group of coproducts, that also include hexachlorobutadiene, hexachloroethane, and hexachlorobenzene.

In another methane chlorination process, the reactants are brought into contact with a fluid catalyst bed, maintained at about 300°C by the heat of the chlorination reaction. The crude product contains approximately equal quantities of carbon tetrachloride and perchloroethylene. Recycle streams sent to the reactor suppress the formation of unwanted coproducts by mass action.

b. Production from carbon disulfide and chlorine:[9]

(1) Process flow diagram: A process flow diagram is shown in Figure 12 below:



(Adapted from a schematic in Reference 9)

Figure 12 - Production Schematic for Carbon Tetrachloride by Reaction of Carbon Disulfide with Chlorine

(2) Process description: A solution of carbon disulfide in carbon tetrachloride (approximately 40% carbon disulfide, 50% carbon tetrachloride, and 10% sulfur monochloride) is charged into a chlorinator equipped with cooling coils. Chlorine is bubbled through the solution, which contains iron powder added as a catalyst. The chlorination temperature is maintained at 30°C.

The reaction products consist primarily of carbon tetrachloride (60%) and sulfur monochloride (40%) and are passed to a distilling column, where they are separated. The carbon tetrachloride distillate is sent to a neutralizer and dryer and the sulfur monochloride is recycled. The low reaction temperature in this process is not considered to be amenable to the formation of by-product HCB or HCBD.

(3) Reactions:

$$CS_2 + 3Cl_2 \xrightarrow[\text{Catalyst}]{\text{Fe}} S_2Cl_2 + CCl_4$$

$$CS_2 + 2S_2Cl_2 \longrightarrow 6S + CCl_4$$

$$6S + 3C \longrightarrow 3CS_2$$

90% Yield

(4) Raw materials:

Basis--1 ton carbon tetrachloride

Carbon disulfide	1,100 lb
Chlorine	2,300 lb

5. Perchloroethylene: Numerous routes are available for manufacture of perchloroethylene according to three broad categories: (a) the dehydrochlorination of pentachloroethane derived from acetylene; (b) direct processes based on acetylene or its chlorination products; and (c) the cracking of other chlorohydrocarbons. Some processes typical of these categories are described below.

a. Production from propane, methane or ethane: One industry source has estimated that approximately 40% of perchloroethylene production in 1970 was based on ethane and propane. A process based on propane is described below.

(1) Production from propane:[9]

(a) Process flow diagram: A process flow diagram is shown in Figure 13.

(b) Process description: Chlorine, propane, and recycled distillation bottoms are mixed and fed to a chlorination furnace held at 900 to 1200°F. Chlorination of the hydrocarbon takes place readily, producing carbon tetrachloride and perchloroethylene. The perchloroethylene is formed largely by pyrolysis of the carbon tetrachloride. Effluent gases from the chlorination furnace are oil-quenched, and the chlorinated hydrocarbons are separated from the quenching medium in a blowback column. The chlorocarbon mixture is then fractionated with the carbon tetrachloride going overhead to recovery and the distillation bottoms routed back to the furnace as recycle. Crude perchloroethylene is purified by distillation and the bottoms are also recycled to the chlorination furnace. The process by-products are carbon tetrachloride (CCl_4) and hydrogen chloride (HCl). There is a strong potential for the formation of HCB and HCBD in the chlorination step; these coproducts concentrate in the still bottoms ("hex wastes").

(c) Reactions:

$$C_3H_8 + 8\ Cl_2 \longrightarrow CCl_2{=}CCl_2 + CCl_4 + 8\ HCl$$

Propane + Chlorine ⟶ Perchloroethylene + Carbon Tetrachloride + Hydrogen Chloride

$$2\ CCl_4 \xrightarrow[\text{88\% yield}]{\text{pyrolysis}} CCl_2{=}CCl_2 + 2\ Cl_2$$

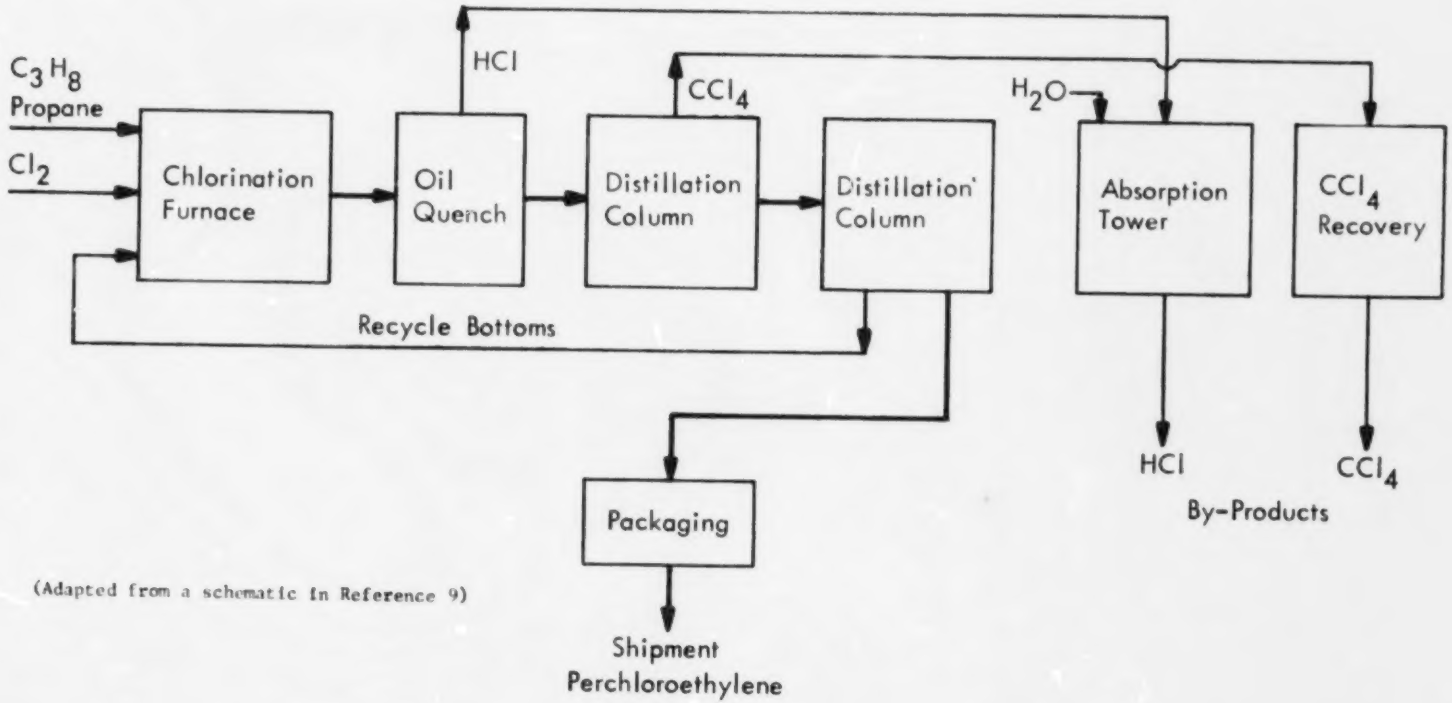
(d) Raw materials:

Basis: 1 ton of perchloroethylene and 2,700 lb hydrogen chloride

Propane	400 lb
Chlorine	5,000 lb

(e) Resource requirements:

Water (cooling)


C_3H_8
Propane
Cl_2
Chlorination Furnace
Oil Quench
HCl
Distillation Column
CCl_4
Distillation Column
Recycle Bottoms
H_2O
Absorption Tower
CCl_4 Recovery
HCl
CCl_4
By-Products
Packaging
Shipment
Perchloroethylene

(Adapted from a schematic in Reference 9)

Figure 13 - Production Schematic for Perchloroethylene from Methane, Ethane, or Propane

(f) By-products and wastes:

Hydrogen chloride

Carbon tetrachloride

Potential discharge of HCB and HCBD from chlorination furnace

The HCBD formed averages a few percent (e.g., up to 2%) of product production.[8] HCB is generally formed as a minor contaminant in the waste.

(2) Production from ethylene dichloride[4]

(a) Process description: Industry sources estimate that approximately 50% of the per chloroethylene production in 1970 was based on ethylene dichloride (trichloroethylene may be coproduced with the per chloroethylene). Chlorination of ethylene dichloride at 300 to 500°C over coke or pumice gives perchloroethylene as the principal product. HCB and HCBD can be formed in this chlorination reaction; these coproducts tend to accumulate in the "hex waste" from the stills.

(b) Reaction: The chemical reaction may be represented as follows:

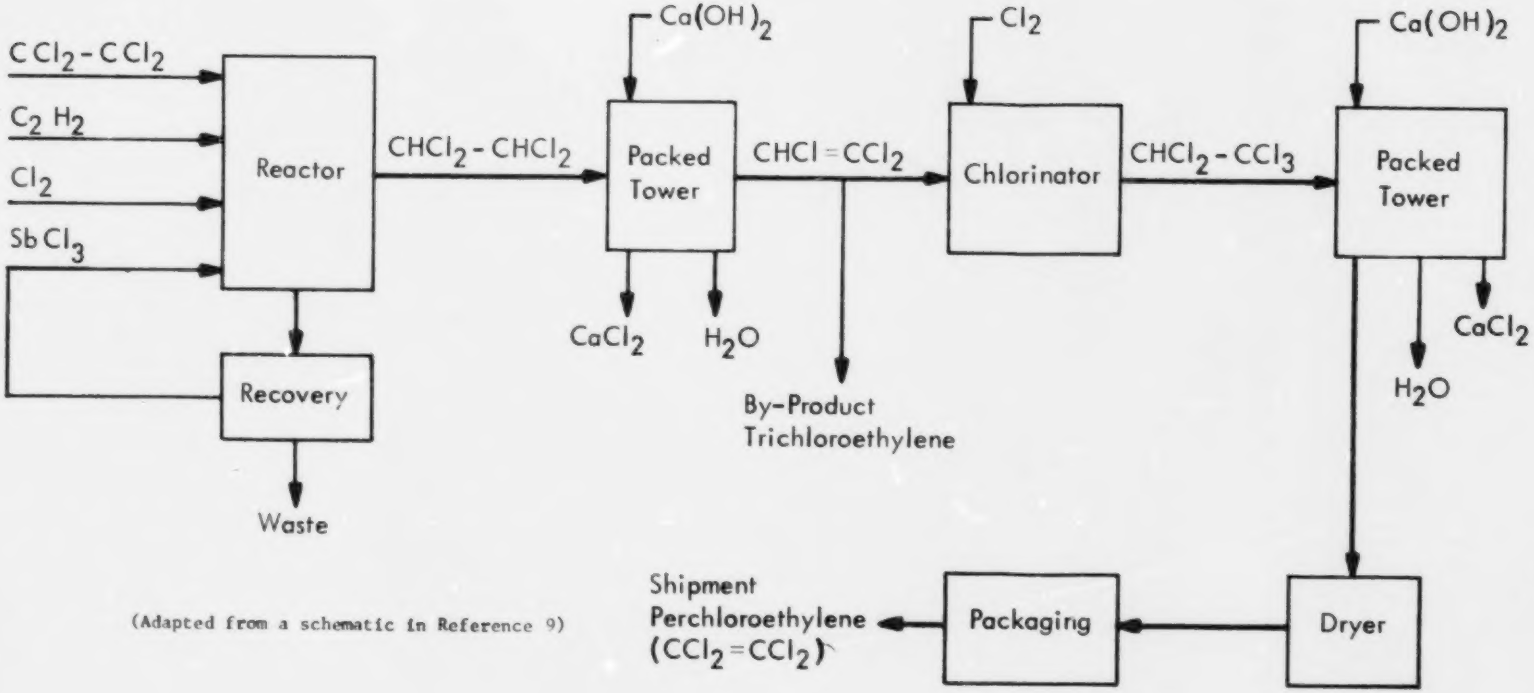
$$CH_2ClCH_2Cl + 3\ Cl_2 \longrightarrow CCl_2{=}CCl_2 + 4\ HCl$$

$$\text{Ethylene Dichloride} \longrightarrow \text{Perchloroethylene} + \text{Hydrogen Chloride}$$

(3) Production from acetylene[9]

(a) Process flow diagram: A process flow diagram is shown in Figure 14.

(b) Process description: Chlorination of acetylene (C_2H_2) is carried out in a reactor in the presence of a catalyst (antimony trichloride, $SbCl_3$) to form tetrachloroethane ($CHCl_2CHCl_2$). The tetrachloroethane is then reacted with calcium hydroxide [$Ca(OH)_2$] to produce trichloroethylene and by-product calcium chloride ($CaCl_2$). The trichloroethylene is then treated with chlorine to form pentachloroethane ($CHCl_2CCl_3$). Pentachloroethane is reacted with calcium hydroxide to produce perchloroethylene ($CCl_2{=}CCl_2$) and by-product calcium chloride. The perchloroethylene is dried and packaged for shipment. In 1972 only 5% of U.S. production was based on this processing method.


CCl_2-CCl_2
C_2H_2
Cl_2
$SbCl_3$
Reactor
Recovery
Waste
$CHCl_2-CHCl_2$
$Ca(OH)_2$
Packed Tower
$CaCl_2$
H_2O
$CHCl=CCl_2$
By-Product Trichloroethylene
Cl_2
Chlorinator
$CHCl_2-CCl_3$
$Ca(OH)_2$
Packed Tower
H_2O
$CaCl_2$
Dryer
Packaging
Shipment Perchloroethylene ($CCl_2=CCl_2$)

(Adapted from a schematic in Reference 9)

Figure 14 - Production Schematic for Perchloroethylene from Acetylene

(c) Reactions:

$$HC{=}CH + 2\ Cl \longrightarrow CHCl_2CHCl_2$$

Acetylene + Chlorine ⟶ 1,1,2,2-tetrachloroethane

$$2\ CHCl_2CHCl_2 + Ca(OH)_2 \longrightarrow 2\ CHCl{=}CCl_2 + CaCl_2 + 2\ H_2O$$

Tetrachloroethane + Calcium Hydroxide ⟶ Trichloroethylene + Calcium Chloride

$$2\ CHCl{=}CCl_2 + 2\ Cl_2 \longrightarrow 2\ CHCl_2CCl_3$$

Trichloroethylene ⟶ Pentachloroethane

$$2\ CHCl_2CCl_3 + Ca(OH)_2 \longrightarrow 2\ CCl_2{=}CCl_2 + CaCl_2 + 2\ H_2O$$

Pentachloroethane ⟶ Perchloroethylene

(d) Raw materials:

Basis: 1 ton perchloroethylene

Acetylene	380 lb
Chlorine	3,000 lb
Calcium hydroxide	900 lb
Catalyst loss	Small

(e) Resource requirements

Water (cooling and process)

(f) By-products and wastes:

Trichloroethylene

Calcium chloride

Waste from perchloroethylene decanter and drier

6. Trichloroethylene

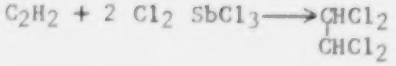
a. Production from acetylene using catalytic dehydrochlorination[9]

(1) Process flow diagram: A process flow diagram is shown in Figure 15.

(2) Process description: Acetylene and chlorine are reacted (at 80 to 100°C) in the presence of tetrachloroethylene and a catalyst (antimony chloride, $SbCl_3$) to produce tetrachloroethane ($Cl_2HC \cdot CHCl_2$).

The tetrachloroethane prepared by this chlorination reaction is vaporized and sent to a catalytic reactor where it is dehydrochlorinated to produce trichloroethylene and hydrogen chloride. The standard catalyst is barium chloride (30%) deposited on carbon. The reactor is heated to 250 to 300°C to maintain the required pyrolysis reaction. Product gases containing 90% trichloroethylene (TCE) and 10% tetrachloroethane are condensed, degassed to remove by-product HCl, and then sent to distillation columns to separate TCE from the heavy ends. A small amount of trimethylamine (20 ppm by weight) or proprietary neutral inhibitors (such as pyrrole-based compounds) may be added to the product to stabilize it. The overall process yield based on either acetylene or chlorine is 90%. This is the only production process which appears to have a significant potential for the formation of by-product HCB and HCBD.

(3) Reactions:

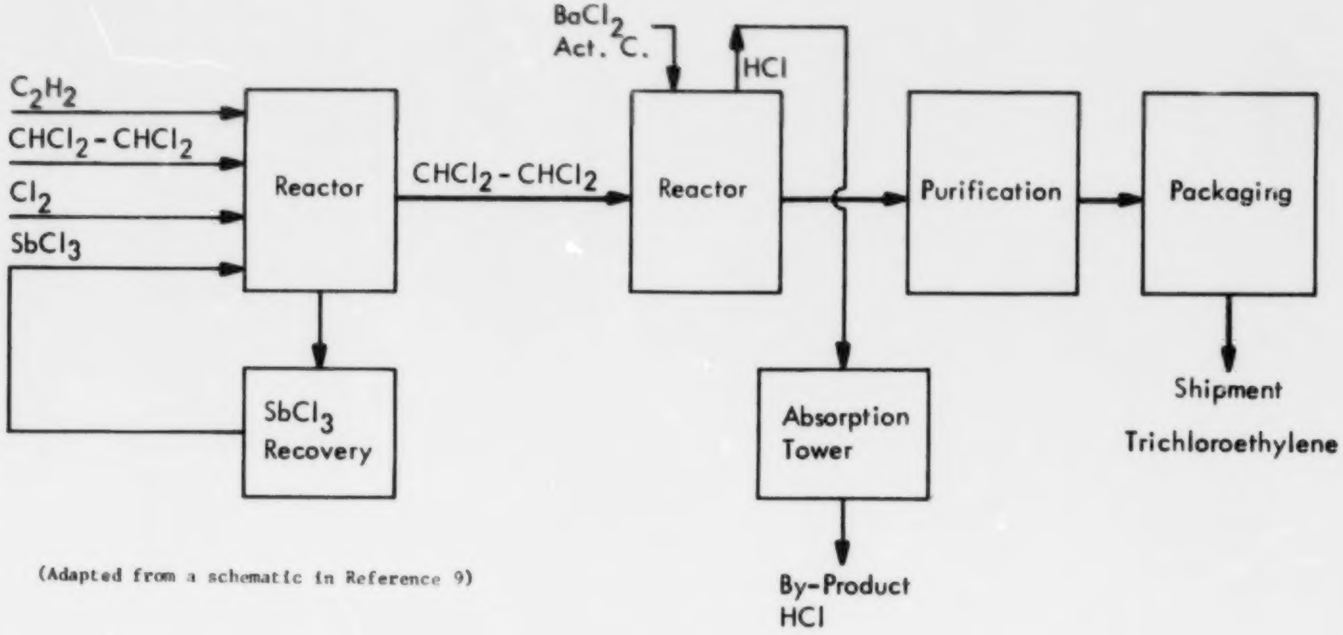


$$C_2H_2 + 2\ Cl_2 \xrightarrow{SbCl_3} \begin{array}{l} CHCl_2 \\ | \\ CHCl_2 \end{array}$$

Acetylene + Chlorine ⟶ Tetrachloroethane

$$CHCl_2 \cdot CHCl_2 \xrightarrow{catalyst} ClHC{=}CCl_2 + HCl$$

Tetrachloroethane ⟶ Trichloroethylene + Hydrogen Chloride


C_2H_2
$CHCl_2-CHCl_2$
Cl_2
$SbCl_3$
Reactor
$SbCl_3$ Recovery
$CHCl_2-CHCl_2$
$BaCl_2$ Act. C.
HCl
Reactor
Absorption Tower
By-Product HCl
Purification
Packaging
Shipment
Trichloroethylene

(Adapted from a schematic in Reference 9)

Figure 15 - Production Schematic for Trichloroethylene from Acetylene Using Catalytic Dehydrochlorination

(4) Raw materials:

Basis: 1 ton of trichloroethylene

Acetylene	440 lb
Chlorine	2,400 lb
Catalyst loss	Small

(5) Resource requirements:

Water (cooling)

(6) By-products and wastes:

Hydrogen chloride

Heavy ends from TCE purification still (waste)

Potential for formation of hexachlorobenzene in the pyrolysis step

b. Production from acetylene using milk of lime[4]

(1) Process flow diagram: A schematic production flow sheet is shown in Figure 16 (page 49).

(2) Process description: The method for providing the intermediate, tetrachloroethane, is identical to that described in Process 1.

In this process the conversion of tetrachloroethane to trichloroethylene is accomplished by contact with a milk of lime, $Ca(OH)_2$, suspension in a packed tower. The trichloroethylene distills overhead and is then condensed, purified, and packaged for shipment.

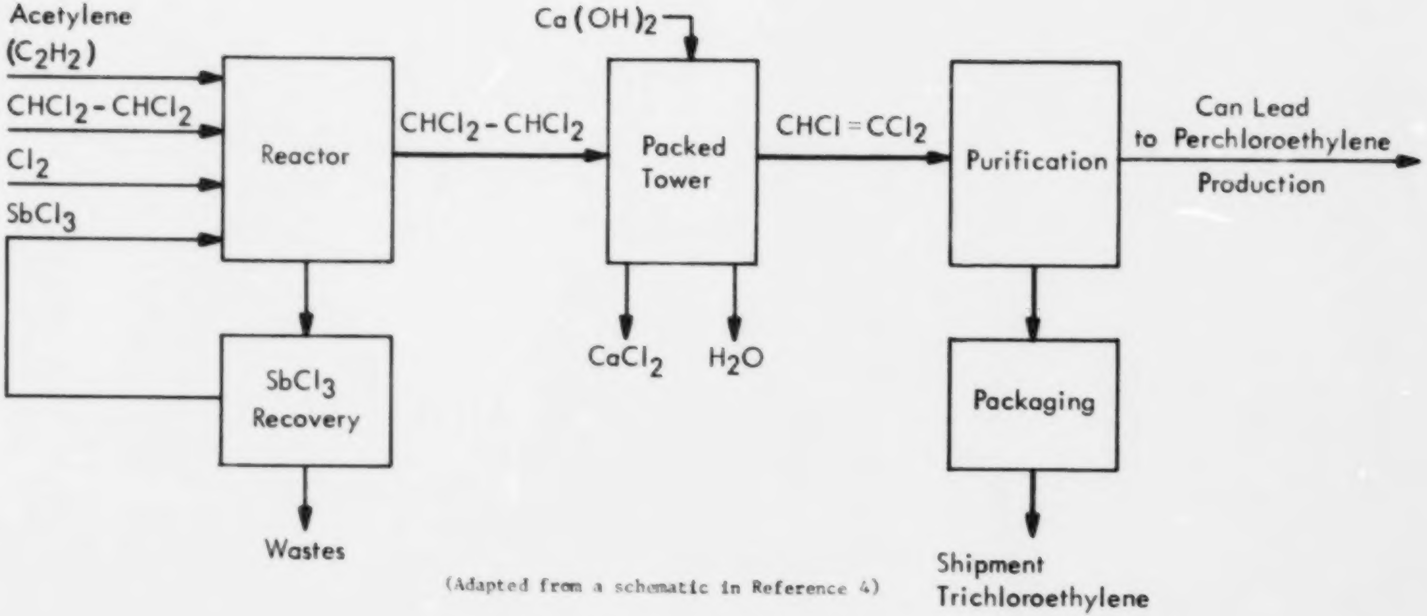
(3) Reactions:

$$HC{\equiv}CH + 2\ Cl_2 \longrightarrow CHCl_2CHCl_2$$

1,1,2,2-tetrachloroethane

$$2\ CHCl_2CHCl_2 + Ca(OH)_2 \longrightarrow 2\ CHCl{=}CCl_2 + CaCl_2 + 2\ H_2O$$

Tetrachloroethane ⟶ Trichloroethylene + Calcium Chloride


Acetylene
(C_2H_2)
$CHCl_2-CHCl_2$
Cl_2
$SbCl_3$
Reactor
$CHCl_2-CHCl_2$
$Ca(OH)_2$
Packed Tower
$CHCl=CCl_2$
Purification
Can Lead to Perchloroethylene Production
$SbCl_3$ Recovery
Wastes
$CaCl_2$
H_2O
Packaging
Shipment Trichloroethylene

(Adapted from a schematic in Reference 4)

Figure 16 - Production Schematic for Trichloroethylene from Acetylene Using Milk of Lime

(4) Raw materials:

Acetylene

Chlorine

Milk of lime

(5) Resource requirements:

Water

(6) By-products and wastes:

Calcium chloride

Wastes from the $SbCl_3$ recovery system

7. Dacthal®: Dacthal® is the proprietary name for dimethyl tetrachloroterephthalate, a herbicide. A processing method described in the patent literature is discussed in the following subsections.

a. Process flow diagram: A process flow diagram is presented in Figure 17.

b. Process description: An improved process route (U.S. Patent No. 3,052,712, September 1962) involves the reaction of hexachloro-p-xylene with terephthalic acid, followed by chlorination of the crude reaction product, and finally, esterification of the crude chlorination product.

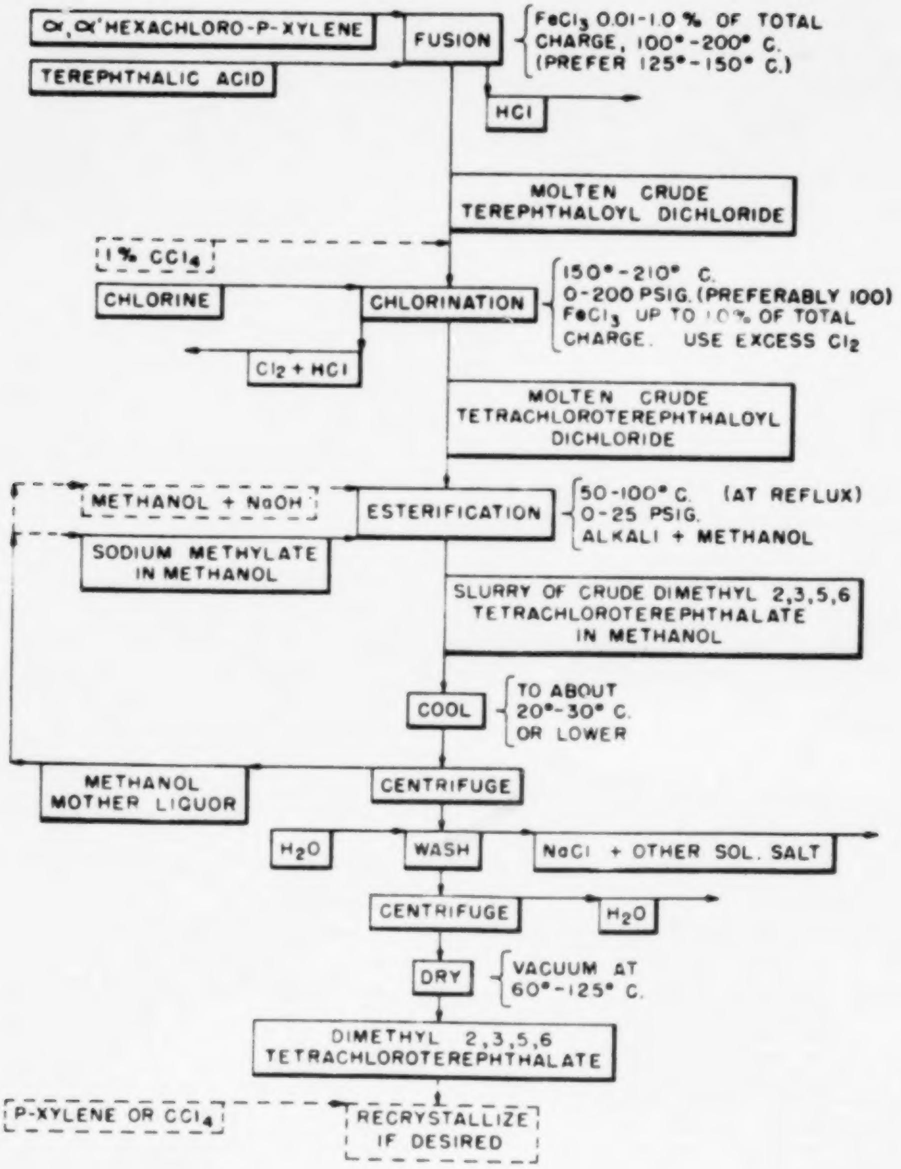
A spokesman[10] for the Diamond Shamrock Corporation, the only domestic producer, has reported that HCB is not an impurity in the feedstock (p-xylene), but is formed in the chlorination reaction. No HCBD is formed in the process. The Dacthal® is reported to contain about 0.3% HCB at present, but apparently contained much higher levels before 1972 (i.e., up to about 10% HCB). Information from a written inquiry (see Appendix B, page 153), shows that waste materials from production of Dacthal® at the only domestic plant contain about 84% of HCB and that the product contains about 0.3% HCB.

c. Reactions:

$$C_6H_4(COOH)_2 + C_6H_4(CCl_3)_2 \longrightarrow 2\ C_6H_4(COCl)_2 + 2HCl$$

$$C_6H_4(COCl)_2 + 4Cl_2 \longrightarrow C_6Cl_4(COCl)_2 + 4HCl$$

$$C_6Cl_4(COCl)_2 + 2CH_3ONa \longrightarrow C_6Cl_4(COOCH_3)_2 + 2NaCl$$


α,α' HEXACHLORO-P-XYLENE
TEREPHTHALIC ACID
FUSION
FeCl3 0.01-1.0 % OF TOTAL CHARGE, 100°-200° C. (PREFER 125°-150° C.)
HCl
MOLTEN CRUDE TEREPHTHALOYL DICHLORIDE
1% CCl4
CHLORINE
CHLORINATION
150°-210° C. 0-200 PSIG. (PREFERABLY 100) FeCl3 UP TO 10% OF TOTAL CHARGE. USE EXCESS Cl2
Cl2 + HCl
MOLTEN CRUDE TETRACHLOROTEREPHTHALOYL DICHLORIDE
METHANOL + NaOH
SODIUM METHYLATE IN METHANOL
ESTERIFICATION
50-100° C. (AT REFLUX) 0-25 PSIG. ALKALI + METHANOL
SLURRY OF CRUDE DIMETHYL 2,3,5,6 TETRACHLOROTEREPHTHALATE IN METHANOL
COOL
TO ABOUT 20°-30° C. OR LOWER
METHANOL MOTHER LIQUOR
CENTRIFUGE
H2O
WASH
NaCl + OTHER SOL. SALT
CENTRIFUGE
H2O
DRY
VACUUM AT 60°-125° C.
DIMETHYL 2,3,5,6 TETRACHLOROTEREPHTHALATE
P-XYLENE OR CCl4
RECRYSTALLIZE IF DESIRED

Source: U.S. Patent 3,052,712

Figure 17 - Flow Diagram for Dimethyl Tetrachloroterephthalate Manufacture

8. **Atrazine:** Atrazine is one of a family of substituted triazine herbicides; the other major members of the group are propazine and simazine. A discussion of the process technology for atrazine is given in the following subsections.

a. Process flow diagrams: A schematic production flow diagram for atrazine is presented in Figure 18, and Figure 19 shows flow diagrams for synthesis of various triazine pesticides.

b. Process description:[11] Cyanogen chloride is first prepared by chlorination of hydrogen cyanide. Cyanuric chloride is then produced by the polymerization of cyanogen chloride in the presence of activated carbon at 350 to 400°C, or in the liquid phase under pressure in various organic solvents with the use of anhydrous aluminum chloride, etc., as catalysts.

The cyanuric chloride is reacted with ethylamine and sodium hydroxide to form 2,4-dichloro-6-ethylamino-S-triazine, which by further reaction with isopropylamine and sodium hydroxide gives atrazine.

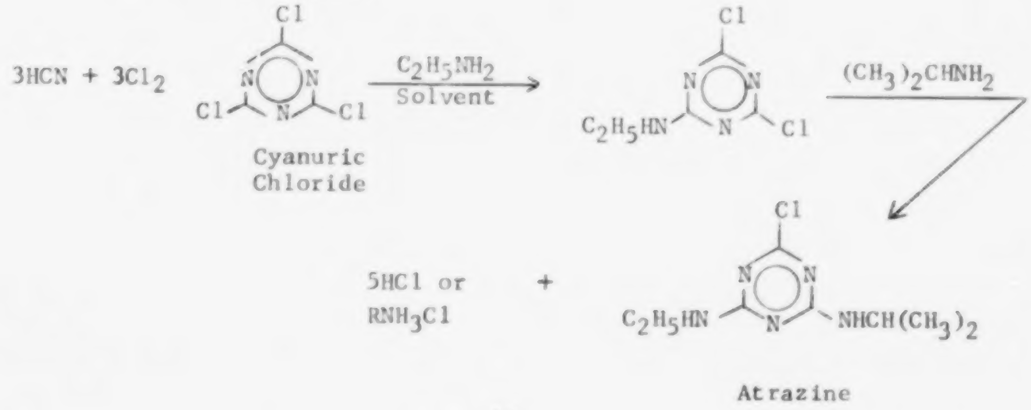
The possible methods for HCB contamination during the production of atrazine are:

- HCB may be contained as an impurity in cyanogen chloride used as intermediate chemical.
- HCB may be formed during the production of cyanuric chloride.

No evidence was found that any HCBD is formed in this industry.

Information obtained by a written inquiry (see pages 145 to 153) shows that atrazine products contain HCB (range of 0.025 to 0.25 ppm) and that the liquid process wastes from the still bottoms also contain HCB (range of 0.024 to 2,000 ppm). HCBD is not produced in the process. Hydrogen chloride, formed as a by-product of the process, is neutralized with caustic soda to form a NaCl waste material.

c. Reactions:



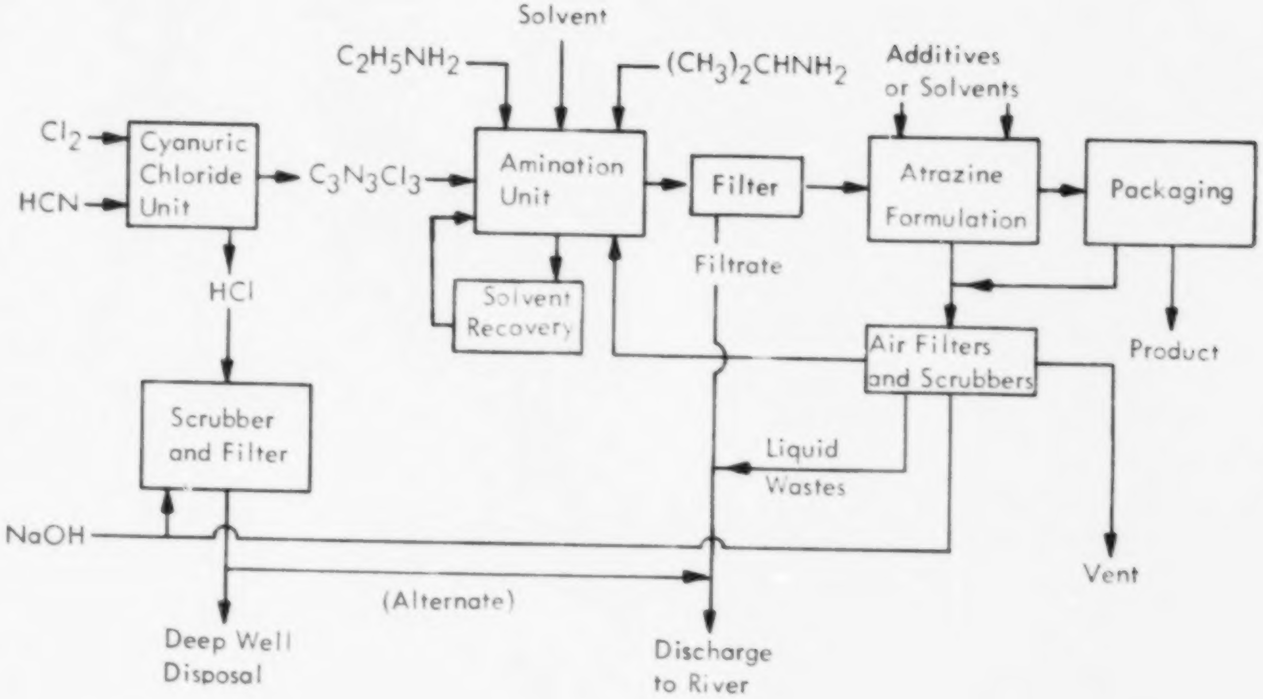

Solvent
$C_2H_5NH_2$
$(CH_3)_2CHNH_2$
Additives or Solvents
Cl_2
HCN
Cyanuric Chloride Unit
$C_3N_3Cl_3$
Amination Unit
Filter
Atrazine Formulation
Packaging
HCl
Filtrate
Solvent Recovery
Air Filters and Scrubbers
Product
Scrubber and Filter
Liquid Wastes
NaOH
Vent
(Alternate)
Deep Well Disposal
Discharge to River

Figure 18 - Production Schematic for Atrazine[11]

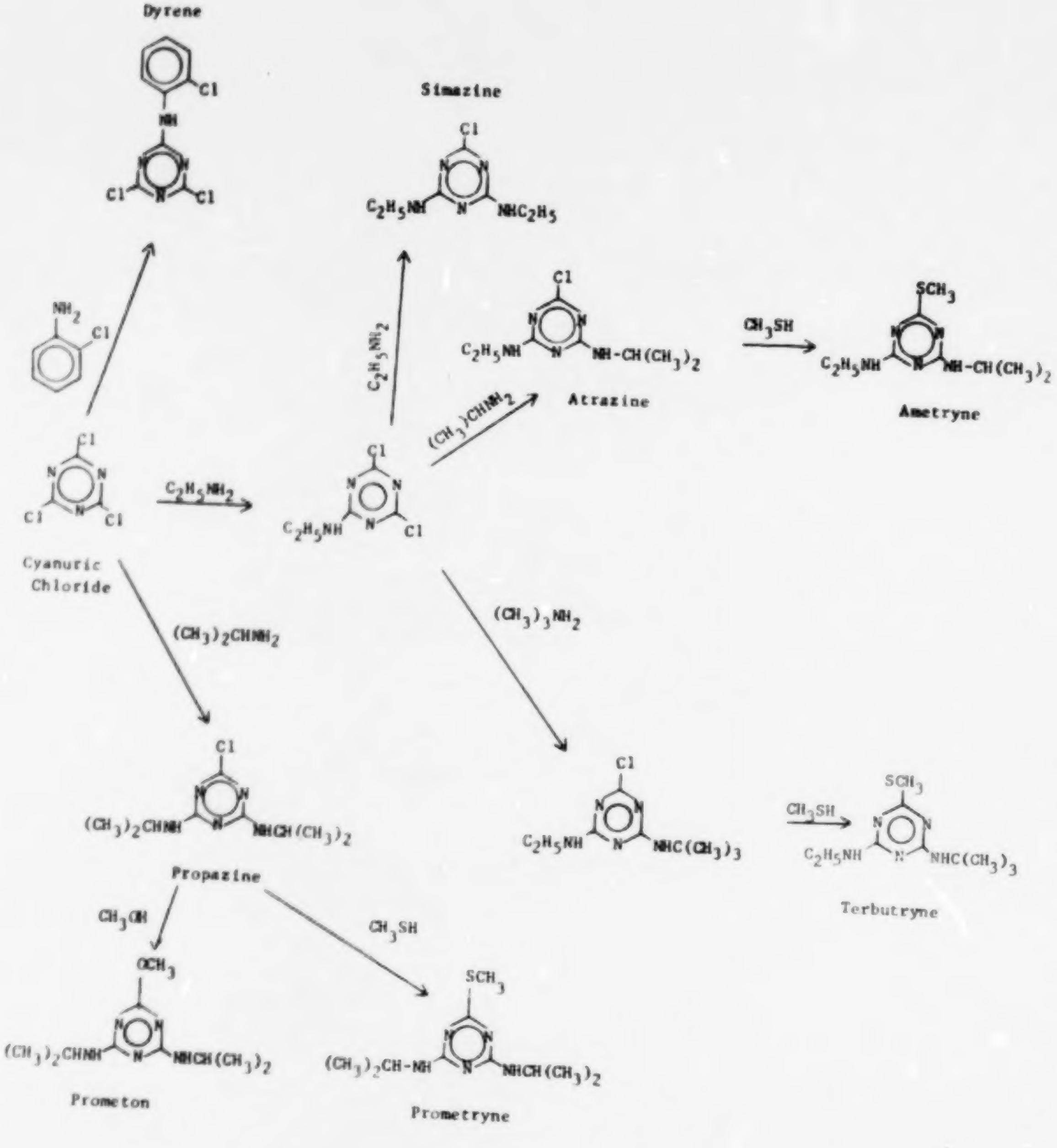

Dyrene
Simazine
Atrazine
Ametryne
Cyanuric Chloride
Propazine
Terbutryne
Prometon
Prometryne
$C_2H_5NH_2$
$(CH_3)_2CHNH_2$
CH_3SH
$(CH_3)_3NH_2$
CH_3OH

Figure 19 - Synthesis of Triazine Pesticides11/

d. Raw materials:

Hydrogen cyanide

"Appropriate" amines

Chlorine

Sodium hydroxide

e. By-products and wastes: By-product hydrogen chloride (0.333 lb HCl produced per pound of atrazine).

Liquid wastes from cyanuric chloride productions unit.

9. Propazine

Process description: Propazine (i.e., the common name for 2-chloro-4,6-bis-isopropylamino-1,3,5-triazine) is synthesized by the reaction of cyanuric chloride with isopropylamine in the presence of an acid acceptor. The technical product is more than 95% pure (molecular formula is $C_9H_{16}N_5Cl$). The process and the prospects for HCB formation are similar to those discussed for atrazine, except that the production volume of the latter is much greater (see page 153 for data from a written inquiry).

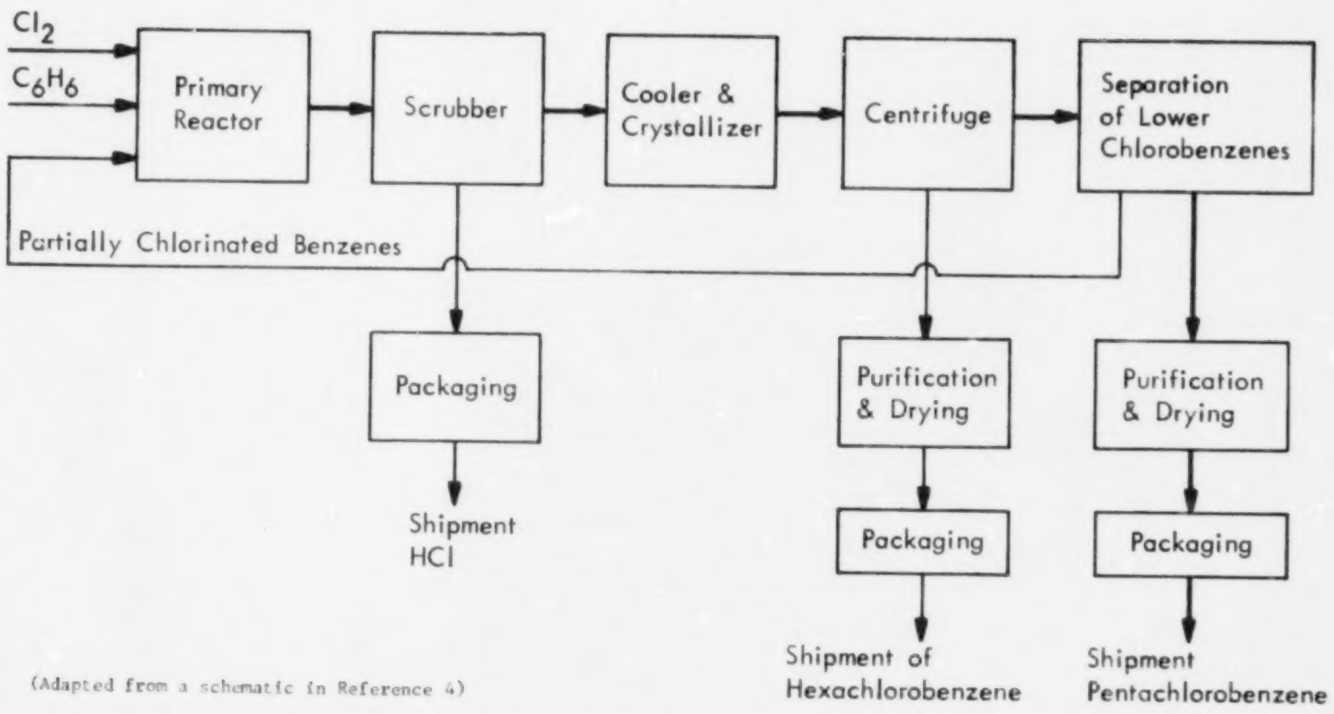
10. Simazine

Process description: Simazine (i.e., the common name for 2-chloro-4,6-bis(ethylamino)-S-triazine) is synthesized by reacting cyanuric chloride with ethylamine in the presence of an acid acceptor. The process and the potential for HCB formation is similar to that for atrazine (see page 153 for data from a written inquiry).

11. Pentachlorobenzene: A discussion of a domestic process for production of pentachlorobenzene is presented in the following subsections.

a. Process flow diagram: A schematic production flow diagram is shown in Figure 20.

b. Process description:[4] Pentachlorobenzene (C_6HCl_5) may be produced by reacting chlorine (Cl_2) with benzene (C_6H_6) or partially chlorinated benzenes (C_6H_5Cl to $C_6H_2Cl_4$) in the presence of a catalyst, ferric chloride ($FeCl_3$), at a temperature of 150 to 200°C. The reaction products are scrubbed with water to remove hydrogen chloride (HCl) to produce by-product hydrochloric acid. The scrubber reaction products are then


Cl_2
C_6H_6
Primary Reactor
Scrubber
Cooler & Crystallizer
Centrifuge
Separation of Lower Chlorobenzenes
Partially Chlorinated Benzenes
Packaging
Shipment HCl
Purification & Drying
Packaging
Shipment of Hexachlorobenzene
Purification & Drying
Packaging
Shipment Pentachlorobenzene

(Adapted from a schematic in Reference 4)

Figure 20 - Production Schematic for Pentachlorobenzene by Chlorination of Benzene or Chlorobenzene

cooled causing hexachlorobenzene (HCB, formula C_6Cl_6) to crystallize out. HCB which is formed as a by-product, is removed by centrifuging or filtering. Pentachlorobenzene separation from the less chlorinated benzenes (C_6H_5Cl to $C_6H_2Cl_4$) and purification is effected by freezing point and solvent extraction methods. The less chlorinated benzenes may be recycled or become by-products.

Small quantities of pentachlorobenzene are produced as a captive by-product in the U.S. The manufacturing process involves some risk of HCB emission to the environment. Because of the captive production, however, it is considered unlikely that any serious HCB pollution problem is created during production of pentachlorobenzene.

c. Reaction:

$$C_6H_6 + 5Cl_2 \xrightarrow[FeCl_3]{150\text{-}200^\circ C} C_6HCl_5 + 5HCl$$

d. Raw materials:

Benzene

Chlorine

Ferric chloride (catalyst)

e. Resource requirements:

Water

f. By-products and wastes:

Hexachlorobenzene

Monochlorobenzene (normally recycled in process)

Dichlorobenzenes (normally recycled in process)

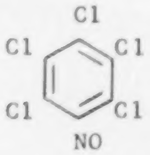
Trichlorobenzenes (normally recycled in process)

Tetrachlorobenzenes (normally recycled in process)

Hydrochloric acid

12. Pentachloronitrobenzene:[6] Pentachloronitrobenzene (PCNB, formula $C_6Cl_5NO_2$) is synthesized by nitrating hexachlorobenzene or chlorinating various chloronitrobenzenes that are formed as by-products in the production of m-chloronitrobenzene and 3,4-dichloronitrobenzene. The chlorination is conducted in the presence of an iron-iodine catalyst. The complete absence of moisture is an important condition for the chlorination, since even a trace of water sharply decreases the rate of the reaction.

The structural formula for PCNB is:


Cl
Cl
Cl
Cl
Cl
NO

13. Mirex: Mirex is a trade name for dodecachloro-octahydro-1,3,4-metheno-2H-cyclobuto(cd)pentalene. The production of this pesticide is described in the following subsections.

a. Process flow diagram: A schematic production flow diagram is shown in Figure 21 below.

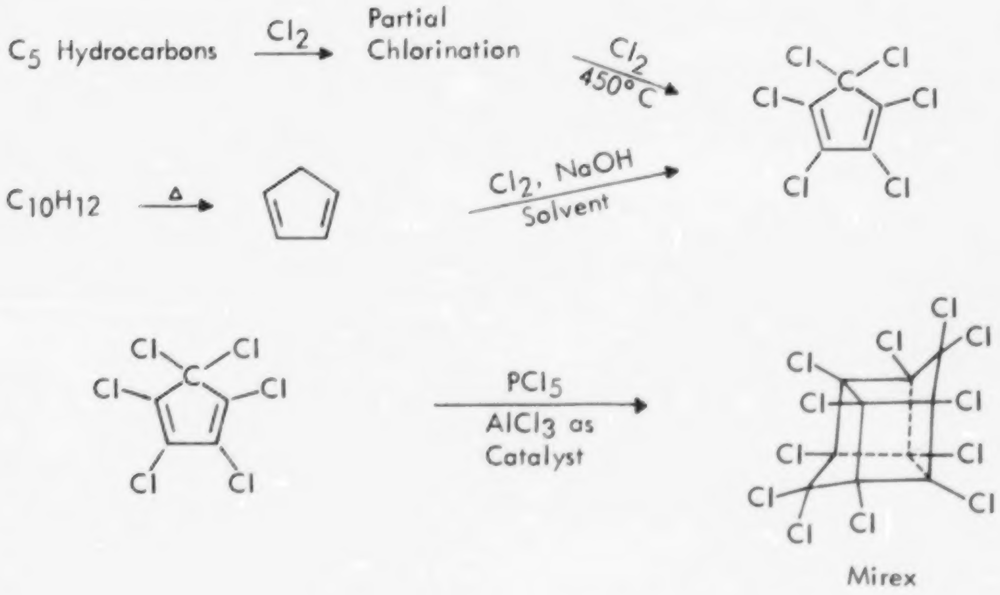

C5 Hydrocarbons
Cl2
Partial Chlorination
Cl2
450°C
C10H12
Δ
Cl2, NaOH
Solvent
PCl5
AlCl3 as Catalyst
Mirex

Figure 21 - Schematic of Reactions for Production of Mirex

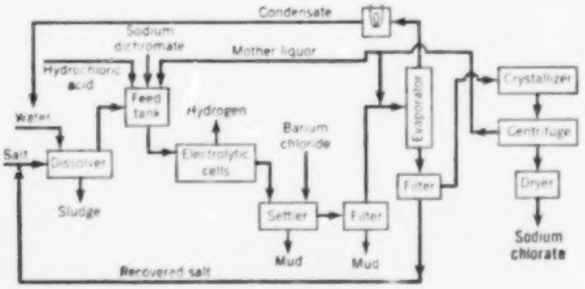
b. Process description: A dimer of hexachlorocyclopentadiene is first prepared by a process (U.S. Patent Re-Issue No. 24,397, 15 February 1955), in which phosphorus pentachloride (PCl_5) is reacted with decachlorotetrahydro-4,7-methanoindene. The Mirex is obtained by a condensation of hexachlorocyclopentadiene dimers.

Hexachlorobenzene contamination could occur in the PCl_5 treatment step of this process. There is also a possibility that feed materials could contain HCB as an impurity.

B. Processes with Theoretical, But Not Proven, Production of HCB and/or HCBD

1. Sodium chlorate: This chemical is produced in the United States by the electrolysis of sodium chloride in aqueous solution. A discussion of this process follows.

a. Process flow diagram: A schematic production flow diagram is shown in Figure 22 below.


Condensate
Sodium dichromate
Mother liquor
Hydrochloric acid
Feed tank
Hydrogen
Water
Salt
Dissolver
Electrolytic cells
Barium chloride
Evaporator
Crystallizer
Centrifuge
Filter
Dryer
Sludge
Settler
Filter
Mud
Mud
Sodium chlorate
Recovered salt

(Adapted from a schematic in Reference 9)

Figure 22 - Production Schematic for Sodium Chlorate

b. Process description:[9] Salt (sodium chloride) is charged into a dissolving tank, where it is converted into a saturated solution by the addition of soft water. Generally, some mud and salt impurities collect at the bottom of the dissolver, from which they are periodically discharged. If the salt contains a high percentage of calcium and magnesium salts, it is usually necessary to purify the solution by precipitation, settling, and filtration of the foreign salts.

The clarified saturated salt solution is transferred to a feed tank, where it is mixed with dilute hydrochloric acid. A concentration of about 0.5% acid is usually maintained so that the average pH of the brine solution in the cells will be approximately 6.5. Sodium dichromate (about 0.2%) is added to inhibit cell corrosion caused by the liberated hypochlorous acid (from the hydrochloric acid present).

The saturated acidulated brine is fed into banks of electrolytic cells, operating batchwise or continuously, maintained at 40 to 45°C by cooling water. The construction and operation of the cells vary in different installations. Generally, the cell bodies are constructed of steel and make use of steel cathodes and graphite anodes. There is no diaphragm in the cell, and the electrodes are closely spaced to allow mixing of the products. The electrolysis actually yields chlorine at the anode and sodium hydroxide at the cathode. However, because of the foregoing conditions, good mixing occurs, resulting in the formation of sodium hypochlorite ($NaClO$) and then sodium chlorate ($NaClO_3$). Hydrogen is liberated during the electrolysis and may be either vented or recovered by suitable means.

The cell liquors, after electrolysis, are discharged into a settler. In batch operations, generally 75% of the salt is converted. The liquor in the settler may be heated to 90°C to destroy any residual hypochlorite.

The chromate ions remain in the liquor and protect steel equipment from corrosion further along in the process. Formates or urea may be added to the liquors in the settler to convert the residual hypochlorite to chlorate. Graphite mud from the anodes settles to the bottom of the tank and is periodically removed.

The liquor contains about 50% sodium chlorate. It is decanted from the top of the settler, passed through a sand filter (if necessary), and charged into double-effect evaporators. Here it is concentrated to approximately 70 to 75% sodium chlorate and filtered. The unconverted sodium chloride is less soluble than the chlorate at boiling temperatures and is thrown out of solution. Recovered salt (filter cake) is returned to the dissolver for reuse.

The filtrate is passed into a crystallizer, where it is cooled (below 30°C) to precipitate sodium chlorate crystals. The product is centrifuged, washed, and dried in rotary dryers. The centrifuge mother liquor and first wash liquors are generally returned to the evaporator for subsequent concentration, although periodically they are returned to the cell feed tank for reprocessing.

The dried product is ground to proper mesh size and screened to yield sodium chlorate crystals, which assay about 99.5%. Although the initial conversion of sodium chloride to chlorate ranges from 50 to 75%, the overall yield (based on the salt charged) is about 95%.

Sodium chlorate may be recovered from the cell liquors by other methods than the previously described concentration process. These other procedures include direct crystallization by refrigerative cooling (about 0°C) and salt exchange (isothermal crystallization) where the chlorate is salted out by addition of sodium chloride.

The chief variations in electrolytic processes for sodium chlorate are in recovery of the product from the cell liquors, which may be accomplished by chilling, salting out, or evaporation. The particular method used depends on conditions existing at a given plant. Considerable care must be taken in the operation of any chlorate plant, because of the potential fire and explosion hazard.

c. Reaction:

$$NaCl + 3H_2O \xrightarrow[\text{6 Faradays}]{\text{Electrolysis}} NaClO_3 + 3H_2$$

d. Raw materials:

Sodium chloride, 1,130 lb/ton of sodium chlorate

e. Resource requirements:

Sodium chloride

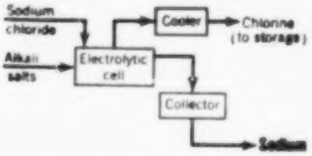
Water

f. Energy requirements

5,100 kw-hr/ton of sodium chlorate

2. Sodium metal: A minor source of chlorine is that produced as coproduct with sodium metal production. Plants producing sodium metal are included in the chlor-alkali listing in Table A-II, Appendix A).

a. Process flow diagram: A schematic production flow diagram is shown in Figure 23 below.



(Adapted from a schematic in Reference 9)

Figure 23 - Production Schematic for Sodium Metal

b. Process description:[9] The electrolysis of salt to produce sodium metal requires very high purity sodium chloride. A pure sodium chloride brine is dissolved in water and treated with sodium hydroxide (to remove heavy metals), barium chloride (to remove sulfate), and ferric chloride (as a coagulant). The brine is evaporated, filtered, and dried.

The pure sodium chloride is mixed with calcium chloride in a Downs Cell to obtain a low-melting fused-salt mixture. The composition is about 58% $CaCl_2$ and 42% NaCl which permits cell operation at 580°C. Additional calcium chloride can be added if lower operating temperatures is desired. The electrolysis produces a sodium-calcium alloy (95% Na, 5% Ca). Upon cooling, most of the calcium precipitates out in the cooled riser pipe. The calcium falls back into the molten salt where it reacts with chlorine to produce calcium chloride.

Sodium metal generated during the electrolysis operation is distilled into a receiver. The material collected is filtered at 110°C. The filtration removes most of the calcium carried over as well as sodium and calcium chloride and oxides. The filtered sodium contains less than 0.04% calcium, and is sufficiently pure for most uses.

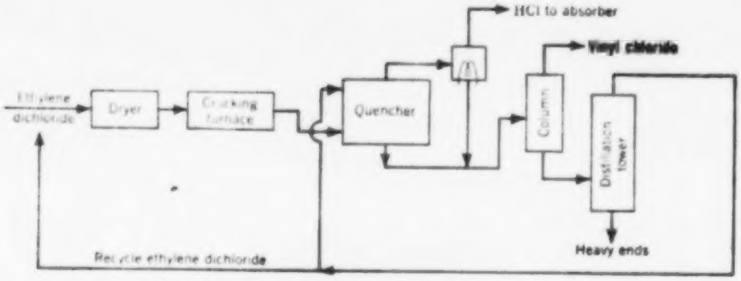
The filter cake produced during the sodium metal recovery is usually solid waste. In some cases, it may contain sufficient chemical reducing power (in the metallic calcium) to serve some specialized needs. The chlorine generated during metallic sodium production is recovered by the same processes and techniques used in the chlor-alkali industry.

No evidence was found that HCB or HCBD are generated in this process.

3. Vinyl chloride monomer: This chemical is produced by: (a) pyrolysis of ethyl dichloride; (b) reaction of ethylene dichloride with caustic soda; and (c) the acetylene process as follows.

a. Production by pyrolysis of ethylene dichloride[9]

(1) Process flow diagram: A schematic production flow diagram is shown in Figure 24 below.



(Adapted from a schematic in Reference 9)

Figure 24 - Schematic for Production of Vinyl Chloride by Pyrolysis of Ethylene Dichloride

(2) Description: Vaporized ethylene dichloride is dried and passed over a contact catalyst (e.g., charcoal or pumice) contained in tubes directly heated in a cracking furnace. At 50 psig, with the effluent gases at 90 to 950°F, a yield of 95 to 96% is attained.

The effluent gases from the furnace are quenched by direct contact with a stream of ethylene dichloride. Uncondensed gases are sent to an indirect condenser to recover the remainder of the condensable vapors and the noncondensables are scrubbed with water to recover hydrogen chloride.

The combined liquid streams from the condenser and quencher are fed to a fractionation tower operated under sufficient pressure to yield vinyl chloride by condensing the overhead vapors in a water condenser. The vinyl chloride is sent to storage. The still bottoms are sent to a still where ethylene dichloride is separated from the "heavy ends" and passed overhead. Condensed ethylene dichloride is recycled, part to the quencher and part to the process feed tank. About 90% of the domestic production of vinyl chloride is accomplished by this process. In this process HCB may be formed in the thermal processing operation.

(3) Reaction:

$$CH_2Cl \cdot CH_2Cl \xrightarrow[95\%\ \text{yield}]{\text{Heat}} CH_2{=}CHCl_2 + HCl$$

(4) Raw materials:

Basis: 1 ton of vinyl chloride

Ethylene dichloride	3,300 lb

(5) By-products and wastes:

HCl (by-product)

The wastes are "heavy ends" (chlorinated tars) from the still.

b. Production by reaction between ethylene dichloride and caustic soda

(1) Process description:[9] A process similar to the pyrolysis process (a) involves heating ethylene dichloride in the presence of caustic soda. Ethylene dichloride is mixed with a water solution containing 6% NaOH in a 2:1 ratio of dichloride to alkali. The mixture is charged to a reactor held at 150 psig where it is allowed to react for 2 to 3 min at 290°F.

The overflow from the reactor is cooled and sent to a pressurized column where vinyl chloride passes overhead to storage. The bottoms are discharged to separate unconverted ethylene dichloride and some water vapor from the valueless bottoms. The ethylene dichloride is separated from accompanying water in a decanter and recycled. The overall yield of vinyl chloride based on ethylene dichloride is 90%.

(2) Reaction:

$$C_2H_4Cl_2 + NaOH \longrightarrow CH_2{=}CHCl + NaCl + H_2O$$

(3) Raw materials

Ethylene dichloride

Sodium hydroxide

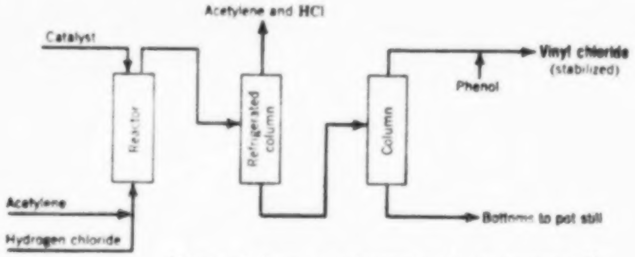
(4) By-products and wastes:

By-products: sodium chloride and water

Wastes: still bottoms (mixture of high boiling organics and brine)

c. Production by the acetylene process[9]

(1) Process flow diagram: A schematic production flow diagram is shown in Figure 25 below.


Acetylene and HCl
Catalyst
Reactor
Refrigerated column
Column
Vinyl chloride (stabilized)
Phenol
Acetylene
Hydrogen chloride
Bottoms to pot still

(Adapted from a schematic in Reference 9)

Figure 25 - Production Schematic for Acetylene Process for Vinyl Chloride

(2) Process description: Dried acetylene (C_2H_2) and anhydrous hydrogen chloride (HCl) are mixed and fed to a reactor containing carbon pellets impregnated with mercuric chloride (catalyst). The reaction is exothermic and the reaction temperature is maintained between 160 and 250°C.

Effluent gases from the reactor are cooled first by heat exchange with cold reactants and finally condensed and fractionated in a refrigerated column from which unreacted C_2H_2 and HCl go overhead. The acid-free monomer or "crude" is further fractionated in a second refrigerated column in which vinyl chloride goes overhead, and by-product ethylidene chloride and aldehydes are removed as bottoms. The condensed vinyl chloride is stabilized with a small amount of phenol and then sent to storage. The yield, based on acetylene, is 99%. Because of the low reaction temperature, it is unlikely that HCB or HCBD is formed in this process.

(3) Reaction:

$$C_2H_2 + HCl \xrightarrow{HgCl_2} C_2H_3Cl$$

(4) Raw materials:

Basis: 1 ton of vinyl chloride

Acetylene	880 lb
Anhydrous hydrogen chloride	1,200 lb

(5) By-products and wastes

Ethylidene chloride and aldehydes are by-products

Wastes include:

- The carbon in the mixing chamber saturated with chlorine and other impurities.
- The spent catalyst suspended in carbon.
- Hydrated solid potassium hydroxide used to dry the product before distillation.

4. Pentachlorophenol:[12/] The principal production process used domestically involves the chlorination of phenol. A discussion of this process follows.

a. Process flow diagram: A schematic production flow diagram is shown in Figure 26.

b. Process description: Pentachlorophenol (PCP, formula C_6Cl_5OH) may be produced by reacting phenol (C_6H_5OH) with chlorine (Cl_2) in the presence of aluminum chloride ($AlCl_3$) at a temperature of 65 to 130°C. The chlorination reactor is of two stage design, the second stage intended to scrub excess Cl_2. Separation of PCP from less chlorinated phenols is effected by melting point. The product is dried for packaging and shipment. Hydrogen chloride (HCl) produced by the process is absorbed by water to produce by-product hydrochloric acid. Less chlorinated phenols may be removed as by-products or recycled.

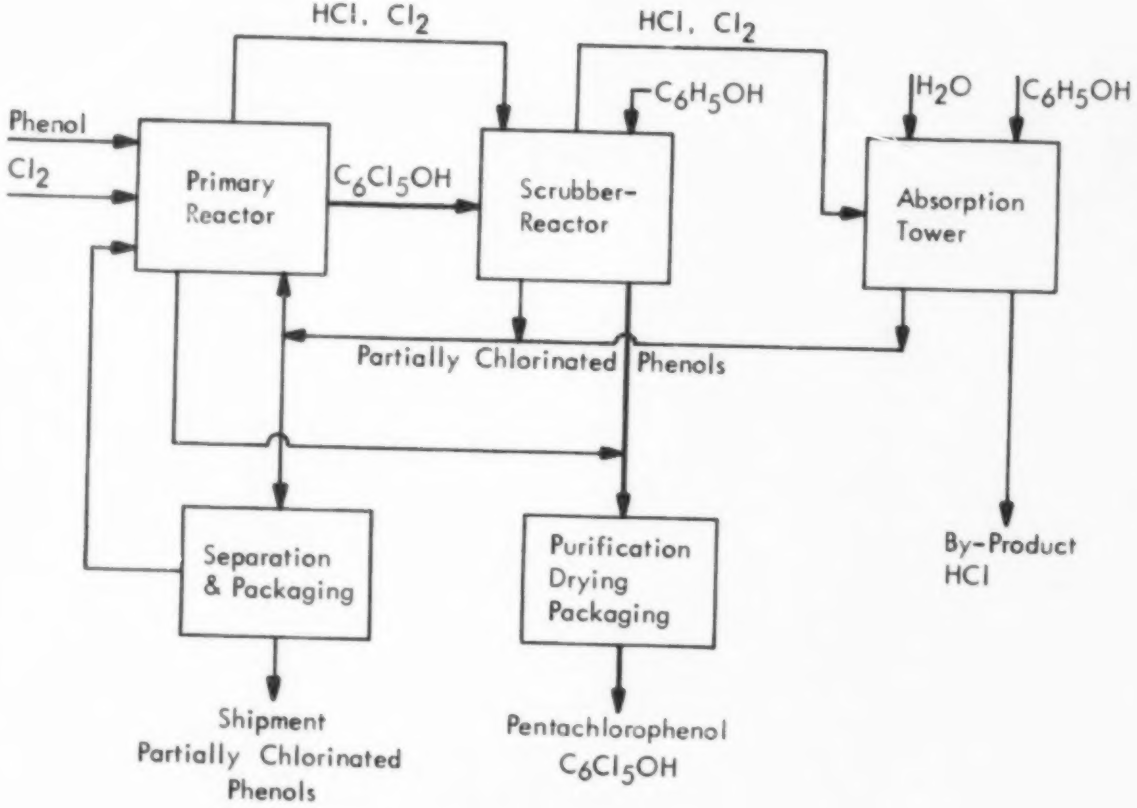

HCl, Cl_2
HCl, Cl_2
Phenol
Cl_2
Primary Reactor
C_6Cl_5OH
C_6H_5OH
Scrubber-Reactor
H_2O
C_6H_5OH
Absorption Tower
Partially Chlorinated Phenols
Separation & Packaging
Purification Drying Packaging
By-Product HCl
Shipment Partially Chlorinated Phenols
Pentachlorophenol C_6Cl_5OH

Figure 26 - Production Schematic for Pentachlorophenol by Chlorination of Phenol[12/]

c. Reaction:

$$C_6H_5OH + 5\ Cl_2 \xrightarrow[AlCl_3]{65\text{-}130^\circ C} C_6Cl_5OH + 5\ HCl$$

d. Raw materials:

Phenol

Chlorine

Aluminum chloride (catalyst)

e. Resource requirements:

Water

f. By-products and wastes:

Hydrogen chloride and the less chlorinated phenols are by-products

5. Hexachloroethane: The most commonly used process for production of this chemical is based on the chlorination of perchloroethylene. A discussion of this process is presented in the following subsections.

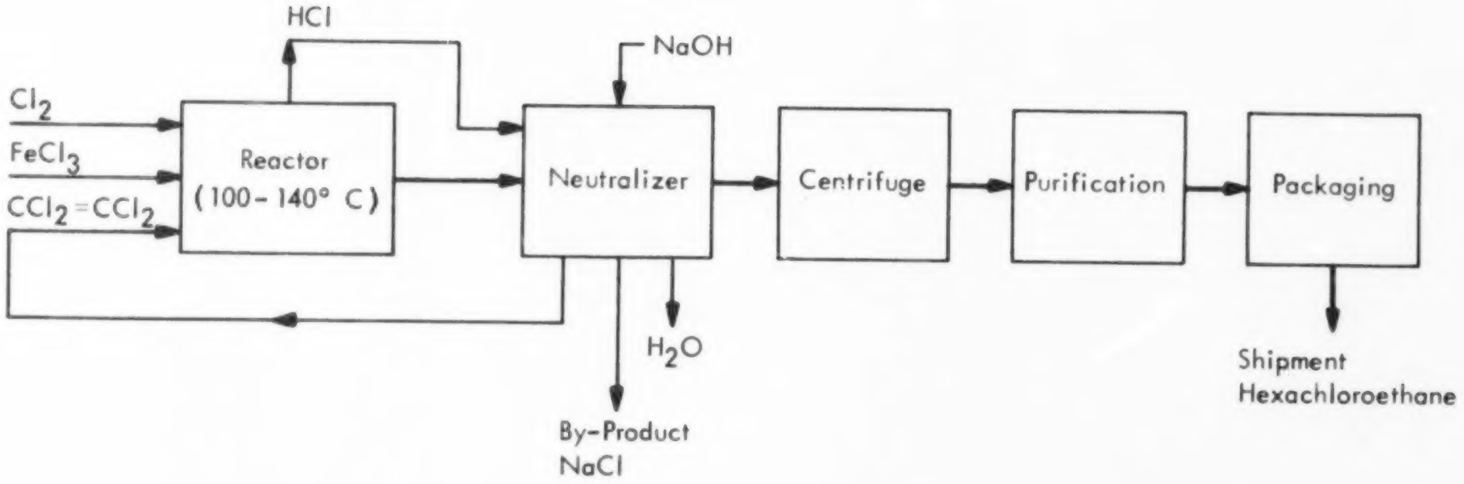
a. Process flow diagram: Figure 27 is a schematic flow diagram for production of hexachloroethane by chlorination of perchloroethylene.

b. Process description:[4] Hexachloroethane (formula C_2Cl_6) is produced by reacting perchloroethylene (C_2Cl_4) with excess chlorine (Cl_2) in the presence of a catalyst, ferric chloride ($FeCl_3$), in a lead-lined vessel at 100 to 140°C. Any hydrogen chloride (HCl) produced is then neutralized with caustic soda (NaOH). The reaction and neutralization products are then cooled. HCE crystallizes, precipitates from solution, and is centrifuged out. The liquid phase is recycled after the water is removed.

Because of the low chlorination temperature, it is unlikely that this process poses any serious problem with regard to HCB or HCBD contamination.

c. Reaction:

$$C_2Cl_4 + Cl_2 \xrightarrow[100\text{-}140^\circ C]{FeCl_3} C_2Cl_6$$


Cl$_2$
FeCl$_3$
CCl$_2$=CCl$_2$
HCl
Reactor (100-140° C)
NaOH
Neutralizer
H$_2$O
By-Product NaCl
Centrifuge
Purification
Packaging
Shipment Hexachloroethane

(Adapted from a schematic in Reference 4)

Figure 27 - Production Schematic for Hexachloroethane from Perchloroethylene

d. Raw materials:

Perchloroethylene

Chlorine

Ferric chloride (catalyst)

Caustic soda

e. Resource requirements:

Water (cooling)

f. By-products and wastes

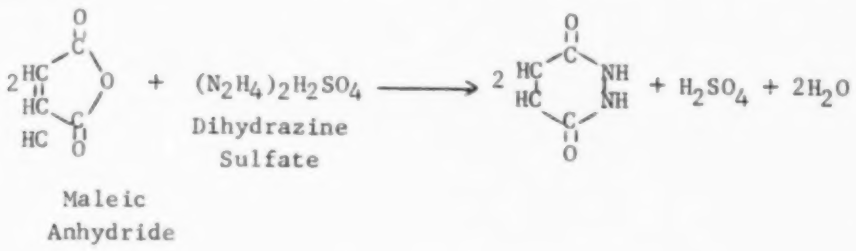
Sodium chloride

Water

6. Synthetic rubber (chloroprene): Of the seven major synthetic rubbers currently produced in the United States, chloroprene production and its polymerization to neoprene appears to present any potential problem in regard to environmental contamination by HCB or HCBD.[4]

Chloroprene is produced by chlorination and dechlorination steps, some of which might produce by-product HCB or HCBD. All of the processing methods are proprietary information, and therefore, no detailed process data could be obtained on the production of chloroprene and its conversion to neoprene. No evidence was found that any of the process operations generate HCB or HCBD.

7. Maleic hydrazide:[4] Maleic hydrazide (3-hydroxypyridazone) is produced by heating equimolecular quantities of hydrazine salts and maleic acid or maleic anhydride in aqueous solution. A typical production reaction is:



Generally the operation is carried out by mixing the reactants and then heating to 75 to 110°C until the reaction has attained the required degree of completion. After cooling, the product precipitates from the mixture and is readily recovered by filtration and washing.

The principal possibility for HCB contamination in this process would be by its introduction as an impurity in one of the raw materials used. Since the maleic anhydride is conveniently made by air oxidation of benzene, it does not appear to be a potential source. Hydrazine (NH_2NH_2) is prepared by reacting elemental chlorine with caustic soda to form NaOCl, forming NH_3Cl by oxidation of ammonia and finally reacting ammonia with NH_2Cl. If hydrazinium chloride ($N_2H_4 \cdot HCl$) were used in place of the sulfate, the HCB might be formed in the reaction itself, but no data on such a reaction were found.

8. Hexachlorocyclopentadiene:[4] Hexachlorocyclopentadiene (HCP) is produced in the United States almost exclusively by the two-stage chlorination of pentane, isopentane or cyclopentane. The first stage is a photochemical chlorination of the hydrocarbon at 80 to 90°C which involves the reaction of 1 mole of hydrocarbon with about 9 moles of chlorine. A crude product (a mixture of noncyclic compounds) with an average formula of $C_3H_5Cl_7$, is continuously withdrawn and then subjected to a vapor-phase chlorinolysis. In the chlorinolysis, the vaporized polychloropentanes and excess chlorine are passed over a surface active catalyst at 300 to 430°C, and then through a nickel tube at a temperature of 450 to 525°C. Octachlorocyclopentane is produced over the catalyst and is then dechlorinated to HCP by the catalytic action of the nickel. Some information was obtained which establishes a potential for the formation of HCB and HCBD in these processing operations.

Another currently used industrial process involves chlorination of cyclopentadiene with sodium hypochlorite. The low reaction temperature of about 40°C precludes the formation of either HCB or HCBD. The cyclopentadiene is produced on-site by vapor phase cracking of naphtha.

Detailed information concerning these proprietary processes could not be obtained by inquiries to the producers.

9. Chlorinated naphthalenes: The Koppers Company, Inc., the sole producer of chlorinated naphthalenes, uses a proprietary process for the manufacturing operation. Our inquiries to this company did not develop any information on the specific process operations involved. The technical literature[3] reports that chlorination of naphthalene in the presence of a catalyst (e.g., ferric chloride) is used to produce commercial quantities of 1-chloronaphthalene and mixtures of polychloronaphthalenes.

The Koppers Company markets several different products under the trade name of "Halowax." These products contain various amounts of chlorine in the range of 22 to 61%. The products may be either liquids (low chlorine content) or waxlike solids (medium and high chlorine content).

1-Chloronaphthalene is produced industrially by passing chlorine into molten naphthalene and fractionally distilling the product. For the manufacture of higher chlorinated naphthalenes, the naphthalene is generally chlorinated in the presence of ferric or antimony chloride. The initial chlorination temperature is 80°C, and the temperature is slowly raised as the reaction proceeds. The final temperatures may reach about 200°C. The chlorinated product is neutralized by stirring in the molten state with aqueous alkali, washed with water, and dried under vacuum.

10. Chlorinated biphenyls (PCBs):[4/] In the United States, PCBs are manufactured by a single producer, the Monsanto Company, and marketed under the trade name of "Aroclor®." The different PCB products are distinguished by number designations in which the first two digits (12) specify polychlorinated biphenyls and the last two digits indicate the P approximate percentage of chlorine in the mixture. The industrially important PCB products are formed by chlorination of biphenyl to give chlorine contents in the range of 21 to 60%.

The chlorination reaction can be accomplished by batch or continuous chlorination. The type of reactor used and the operating conditions influence the composition of the Aroclor® product in regard to content of isomers and other compounds.

The chlorinators are generally steel towers equipped with chlorine distributors at the bottom, heat transfer coils, and pumps for circulating the liquid. The lower portion of the chlorinator is filled with ferric chloride (catalyst).

For the manufacture of PCBs (1200 series Arochlor®), the chlorinator is charged with biphenyl, and chlorine gas is bubbled through the liquid biphenyl. Throughout the chlorination, the temperature is kept well above the melting point of the mixture, but below 150°C. Anhydrous hydrogen chloride, which is evolved during chlorination is absorbed in water. The time required for chlorination is 12 to 36 hr, depending upon the chlorine content of the product.

C. Methodology and Results of a Study to Estimate Quantities of HCB and/or HCBD Generated by Chemical Industry

This section outlines the methodology and results for MRI estimates of the quantities of HCB and/or HCBD contained in chemical process wastes, by-products, and products. The results apply for 1972.

1. Perchloroethylene and trichloroethylene: The U.S. production of perchloroethylene (perchloro) and trichloroethylene (trichloro) in 1972 was 734,800,000 and 427,000,000 lb, respectively.

Information in the attached table (Table III), shows that the waste quantity and composition varies widely from company to company. Therefore, estimates of the HCB and HCBD generated were prepared for each company, and then summed to obtain the total estimate for each industry. Assume that production for each company corresponds to the percent of total U.S. capacity represented by the company.

a. Diamond Shamrock Company

Perchloro: Production is 11.3% of total or 83.03×10^6 lb, the tar residue is 1% high or 0.5% low (assumed) of product and it contains 10% HCB (assumed) and 75% HCBD.

High HCB = (83.032×10^6) (0.01) (0.10) = 83,032 lb
Low HCB = (0.5) (high) = 41,516 lb

High HCBD = (83.032×10^6) (0.01) (0.75) = 622,740 lb
Low HCBD = (0.5) (high) = 311,370 lb

Trichloro: Production is 11.3% of total or 48.251×10^6 lb, the tar residue is 1% high or 0.5% low (assumed) of product and contains 10% HCB and 75% HCBD.

High HCB = (48.251×10^6) (0.01) (0.10) = 48,250 lb
Low HCB = (0.5) (high) = 24,126 lb

High HCBD = (48.251×10^6) (0.01) (0.75) = 361,880 lb
Low HCBD = (0.5) (high) = 180,940 lb

b. Dow Chemical Company

Perchloro: Production is 27.7% of total or 203.5396×10^6 lb. Assume the tar residue produced is 1% high and 0.5% low of product and that the residue contains 15% HCB and 70% HCBD.

TABLE III

PRODUCTION AND WASTE DISPOSAL DATA (1973) FOR PERCHLOROETHYLENE AND TRICHLOROETHYLENE

Company	Location	Products	Capacity[a] MM lb/yr 1972		Waste or By-Product Composition	Waste Disposal	Remarks
Diamond Shamrock Chemical Company	Deer Park, Texas	Perchloro Trichloro	100	 60	75% HCBD, 10% HCB, plus other chlorobutadienes	Ship to Rollins for incineration. Gases from latter scrubbed with NaOH and dumped without treatment.	Tar is 1% of product output
Dow Chemical Company	Freeport, Texas	Perchloro Trichloro	120	 150	NA NA	Company prefers not to identify past or current methods but incinerators comparable to Plaquemine are either planned or under construction.	
	Pittsburg, California	Perchloro --	20	 --			
	Plaquemine, Louisiana	Perchloro --	105		70% HCBD, 5-15% HCE,[b] remainder HCB	Incineration with loss to environment of less than 11 lb/day.	
E. I. du Pont de Nemours and Company	Corpus Christi, Texas	Perchloro --	(500)	 --	Unknown	Unknown	Due on stream late 1973 Company claims HCBD, etc., waste will "present no problems."
Ethyl Corporation	Baton Rouge, Louisiana	Perchloro Trichloro	75	 50	66.5% HCBD; 6.3% HCE,[b] 1.0% HCB	Deep well disposal (8,000 ft deep)	Monitor plant and workers for HCB and HCBD.
PPG Industry, Inc.	Lake Charles, Louisiana	Perchloro Trichloro	160	 200	NA NA	Landfill until completion of incinerator in July 1973.	
Stauffer Chemical Company	Louisville, Kentucky	Perchloro --	70	 --	10% HCBD, 80% HCB, HCE, etc.	HCB recovered for sale, remainder recycled to chlorinator.	
Vulcan Materials Company	Geismar, Louisiana	Perchloro --	150	 --	70% HCBD, 20% HCB, HCE, etc.	Geismar disposes under water seal in lagoon. Plan incineration within 2 years. Air above lagoon less than 1 ppb HCBD.	Tar production 5% of perchloro output
Vulcan Materials Company Hooker Chemical Corporation	Wichita, Kansas; Taft, Louisiana	Perchloro Perchloro Trichloro	40 45 ___	 70	35% HCBD, 60% HCB, HCE, etc.	Unknown	
Total			885	530			

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a/ Capacities of some plants are very flexible, since the same equipment is used to make other chlorinated solvents.
b/ Hexachloroethane.
Source: (1) SRI Chemical Economics Handbook (capacity data) 1973.
(2) Industry and government contacts (all other data).

High HCB = (203.9596×10^6) (0.01) (0.15) = 305,939 lb
Low HCB = (0.5) (high) = 152,970 lb

High HCBD = (203.9596×10^6) (0.01) (0.7) = 1,427,717 lb
Low HCBD = (0.5) (high) = 713,859 lb

Trichloro: Production is 28.3% of total or 120.841×10^6 lb. Assume other conditions are the same as for perchloro.

High HCB = (120.841×10^6) (0.01) (0.15) = 181,262 lb
Low HCB = (0.5) (high) = 90,631 lb

High HCBD = (120.841×10^6) (0.01) (0.7) = 845,887 lb
Low HCBD = (0.5) (high) = 422,944 lb

c. Ethyl Corporation

Perchloro: Production is 8.5% of total or 62.458×10^6 lb. Assume the tar is 1% high and 0.5% low of product, and that tar contains 1% HCB and 66.5% HCBD.

High HCB = (62.458×10^6) (0.01) (0.01) = 6,246 lb
Low HCB = (0.5) (high) = 3,123 lb

High HCBD = (62.458×10^6) (0.01) (0.665) = 415,346 lb
Low HCBD = (0.5) (high) = 207,673 lb

Trichloro: Production is 9.4% of total or 40.138×10^6 lb. Assume other conditions are the same as for perchloro.

High HCB = (40.138×10^6) (0.01) (0.01) = 4,000 lb
Low HCB = (0.5) (high) = 2,000 lb

High HCBD = (40.138×10^6) (0.01) (0.665) = 266,900 lb
Low HCBD = (0.5) (high) = 133,450 lb

d. PPG Industry, Inc.

Perchloro: Production is 18.1% of total or 132.999×10^6 lb. Assume the tar is 1% or 0.5% of product and that tar contains 10% HCB and 70% HCBD.

High HCB = (132.999×10^6) (0.01) (0.1) = 133,000 lb
Low HCB = (0.5) (high) = 66,500 lb

High HCBD = (132.999×10^6) (0.01) (0.7) = 931,000 lb
Low HCBD = (0.5) (high) = 465,500 lb

Trichloro: Production is 37.8% of total or 161,406 x 10^6 lb. Assume other conditions are the same as for perchloro.

High HCB = (161.406 x 10^6) (0.01) (0.1) = 161,400 lb
Low HCB = (0.5) (high) = 80,700 lb

High HCBD = (161.406 x 10^6) (0.01) (0.7) = 1,129,900 lb
Low HCBD = (0.5) (high) = 565,000 lb

e. Stauffer Chemical Company

Perchloro: Production is 7.9% of total or 58.049 x 10^6 lb. Assume by-product is 600,000 lb (high) or 300,000 (low) perchloro production and that by-product contains 80% HCB and 10% HCBD.

High HCB = (58.049 x 10^6) (0.0151) (0.8) = 700,000 lb
Low HCB = (0.5) (high) = 350,000 lb

High HCBD = (58.049 x 10^6) (0.0151) (0.10) = 87,700 lb
Low HCBD = (0.5) (high) = 43,900 lb

f. Vulcan Materials Company

Perchloro: At the Geismar, Louisiana, plant the production is 16.9% of total or 124.181 x 10^6 lb. Assume tar production is 5 or 2.5% of perchloro output, and that tar contains 20% HCB and 70% HCBD.

High HCB = (124.181 x 10^6) (0.05) (0.2) = 1,241,800 lb
Low HCB = (0.5) (high) = 620,900 lb

High HCBD = (124.181 x 10^6) (0.05) (0.7) = 4,346,400 lb
Low HCBD = (0.5) (high) = 2,173,200 lb

At the Wichita, Kansas, plant the production is 4.5% of total or 33.066 x 10^6 lb. Assume tar production is 5 or 2.5% of perchloro and that tar contains 60% HCB and 35% HCBD.

High HCB = (33.066 x 10^6) (0.05) (0.6) = 992,000 lb
Low HCB = (0.5) (high) = 496,000 lb

High HCBD = (33.066 x 10^6) (0.05) (0.35) = 578,700 lb
Low HCBD = (0.5) (high) = 289,400 lb

Trichloro: None produced.

g. Hooker Chemical Corporation

Perchloro: Production is 5.1% of total or 37.4748×10^6 lb. Assume the tar residue is 1 or 0.5% of product, and that tar contains 10% HCB and 70% HCBD (assumed composition).

High HCB = (37.4748×10^6) (0.01) (0.1) = 37,500 lb
Low HCB = (0.5) (high) = 18,750 lb

High HCBD = (37.4748×10^6) (0.01) (0.7) = 262,300 lb
Low HCBD = (0.5) (high) = 131,150 lb

Trichloro: Production is 13.2% of total or 56.364×10^6 lb. Assume other conditions are the same as for perchloro.

High HCB = (56.364×10^6) (0.01) (0.1) = 56,400 lb
Low HCB = (0.5) (high) = 28,200 lb

High HCBD = (56.364×10^6) (0.01) (0.7) = 394,500 lb
Low HCBD = (0.5) (high) = 197,250 lb

Table IV presents the summary data for the perchloro and trichloro estimate. These data show the estimated range (high and low values) for HCB and HCBD generation and the estimated percentage distribution of HCB and HCBD by company.

2. Carbon tetrachloride (CCl_4): The U.S. production of CCl_4 in 1972 was 997 million pounds per year. About 60% of this production was by the CS_2 process which precludes the formation of HCB or HCBD.

In the absence of information on the composition of the process hex wastes, and because of the similarity of processing operations, assume that the CCl_4 wastes are identical to the hex wastes produced in perchloroethylene-trichloroethylene production.

Industry spokesmen have reported[15,16] that the tarry hex residue in perchloroethylene-trichloroethylene operations can range in quantity from about 0.5 to 1% of the product depending on the depth of chlorination. Also, the average composition of the hex waste is reported to be about 10% HCB and 70% HCBD.

TABLE IV

SUMMARY OF PERCHLORO/TRICHLORO ESTIMATES

Data For Perchloro Operations in 1972

Company	HCB			HCBD		
	High (10^3 lb)	Low (10^3 lb)	Percent of Total	High (10^3 lb)	Low (10^3 lb)	Percent of Total
Diamond	83.0	41.5	2.37	622.7	311.4	7.18
Dow	305.9	153.0	8.74	1,427.7	713.9	16.46
Ethyl	6.2	3.1	0.18	415.3	207.7	4.79
PPG	133.0	66.5	3.80	931.0	465.5	10.74
Stauffer	700.0	350.0	20.00	87.7	43.9	1.02
Vulcan (1)	1,241.8	620.9	35.49	4,346.4	2,173.2	50.12
Vulcan (2)	992.0	496.0	28.35	578.7	289.4	6.67
Hooker	37.5	18.8	1.07	262.3	131.2	3.02
Total	3,499.4	1,749.8	100.00	8,671.8	4,336.2	100.00

Data For Trichloro Operations in 1972

Company	HCB			HCBD		
	High (10^3 lb)	Low (10^3 lb)	Percent of Total	High (10^3 lb)	Low (10^3 lb)	Percent of Total
Diamond	48.3	24.1	10.70	361.9	180.9	12.07
Dow	181.3	90.6	40.16	845.9	422.9	28.21
Ethyl	4.0	2.0	0.89	266.9	133.5	8.90
PPG	161.4	80.7	35.76	1,129.9	565.0	37.67
Hooker	56.4	28.2	12.49	394.5	197.3	13.15
Total	451.4	225.6	100.00	2,999.1	1,499.6	100.00

The estimated HCB formed is:

High = (0.4) (997,000,000) (0.01) (0.10) = 398,800 lb
Low = (0.4) (997,000,000) (0.005) (0.10) = 199,400 lb

The estimated HCBD formed is:

High = (0.4) (997,000,000) (0.01) (0.70) = 2,791,600 lb
Low = (0.4) (997,000,000) (0.005) (0.70) = 1,395,800 lb

3. Chlorine (Cl_2):

Production in 1972 = 9,873,000 tons of Cl_2.

Diaphragm cells = 72.4% of production capacity.[17]

Mercury cells = 24.2% of production capacity.[17]

Assume that:

63.3% of mercury cells have been converted to DSA.

34.7% of diaphragm cells have been converted to DSA.

The converted cells do not form HCB or HCBD.

Then, total Cl_2 production from polluting mercury cells = (0.242) (1-0.633) (9,873,000 tons/year) = 877,000 tons/year.

And the total Cl_2 production from polluting diaphragm cells = (0.724) (1-0.347) (9,873,000 tons/year) = 4,668,000 tons/year.

Mercury cells

Assume that:

1. The heavy ends waste amounts to 1.4 lb/ton Cl_2.[7] Then, waste chlorinated hydrocarbons = (1.4 lb/ton Cl_2) (877×10^3 ton Cl_2/year) = $1,288 \times 10^3$ lb/year.

2. The crude chlorine and purified chlorine are same quantities (no losses in purification).

3. The waste contains from 2 to 5% HCB, plus varying amounts of HCBD, carbon tetrachloride, and chloroform.[15,18,19]

4. The HCB content of product chlorine ranges from 5 to 1 ppb.[15,19]

HCB in chlorinated hydrocarbon waste stream

High = (0.05 lb HCB/lb waste) (1,228,000 lb waste/year) = 61,400 lb HCB/year

Low = (0.02 lb HCB/lb waste) (1,228,000 lb waste/year) = 24,560 HCB/year

HCB in product chlorine

High = (877×10^3 tons Cl_2/year) (2,000 lb/ton) (5×10^{-9} tons HCB/ton Cl_2) $\simeq$ 9 lb HCB/year

Low = (877×10^3 tons Cl_2 /year) (2,000 lb/ton) (1×10^{-9} ton HCB/ton Cl_2) $\simeq$ 2 lb HCB/year

Total HCB from mercury cells

High = 61,400 + 9 $\simeq$ 61,400 lb HCB/year

Low = 24,560 + 2 $\simeq$ 24,600 lb HCB/year

Diaphragm cells

Assume conditions are the same as in the mercury cell process. Then, the waste chlorinated hydrocarbons = (1.4 lb/ton Cl_2) ($4,668 \times 10^3$ tons Cl_2/year) = $6,535 \times 10^3$ lb/year

HCB in chlorinated hydrocarbon waste stream

High = (0.05 lb/HCB/lb waste) ($6,535 \times 10^3$ lb waste/year) = 326,800 lb HCB/year

Low = (0.02 lb HCB/lb waste) ($6,535 \times 10^3$ lb waste/year) = 130,700 lb HCB/year

HCB in product chlorine

High = (4,668 x 10^3 tons Cl_2/year) (2,000 lb/ton) (5 x 10^{-9} lb HCB/lb Cl_2) = 47 lb HCB/year

Low = (4,668 x 10^3 tons Cl_2/year) (2,000 lb/ton) (1 x 10^{-9} lb HCB/lb Cl_2) = 9 lb HCB/year

Total HCB from diaphragm cells

High = 326,800 + 47 ≃ 326,800 lb HCB/year

Low = 130,700 + 9 ≃ 130,700 lb HCB/year

Total HCB formed in all Cl_2 plants

High = 61,400 + 326,800 = 388,200 lb HCB/year

Low = 24,600 + 130,700 = 155,300 lb HCB/year

Total HCBD formed in all Cl_2 plants

An industry spokesman has reported that HCBD[15] present in waste is less than 1% of the by-product HCBD formed in all domestic perchloroethylene and trichloroethylene plants (i.e., < 1% of 8,130,000 or 81,300 lb/year). Assume 0.5 to 0.9% for a range of values.

High = 8,130,000 x 0.009 = 73,170, say 73,200 tons/year

Low = 8,130,000 x 0.005 = 40,650, say 40,700 tons/year

4. Dacthal®: An industry spokesman[20] has indicated that the total domestic production of Dacthal® in 1972 was 2 million pounds, and that this product contains an average of about 0.3% of HCB and no HCBD. Also, according to this spokesman, the total Dacthal® process wastes in 1972, amounting to about 100,000 lb, contain an average of 84% HCB and no HCBD.

Assume that:

1. The HCB contamination in Dacthal® ranges from a high of 0.4% to a low of 0.2%.

2. The HCB content in Dacthal® process wastes ranges from a high of 88% to a low of 80%.

Then, quantities of HCB formed are:

For Dacthal® product:

High = (2,000,000 lb) (0.004) = 8,000 lb HCB

Low = (2,000,000 lb) (0.002) = 4,000 lb HCB

For HCB contained in wastes:

High = (100,000 lb) (0.88) = 88,000 lb HCB

Low = (100,000 lb) (0.80) = 80,000 lb HCB

Total HCB formed:

High = 8,000 + 88,000 = 96,000 lb

Low = 4,000 + 80,000 = 84,000 lb

5. Vinyl chloride monomer: U.S. production in 1972 = 2,247,000 tons/year, or 4,494,000,000 lb/year.

According to the technical literature, 92% of vinyl chloride production capacity uses the ethylene and ethylene-oxychlorination processes, which involve the high reaction temperatures conducive to formation of HCB.

Industry spokesmen have indicated that HCBD is not formed in the manufacture of vinyl chloride and that heavy ends waste sent to incineration or other disposal is about 6.5% of the product. A potential does exist for the formation of HCB; however, no analytical data on this subject could be obtained.

Assume that heavy ends waste from the process contains a maximum of 0.01% HCB and a minimum of 1 ppm HCB. Then range of HCB formed is:

High = (0.92) ($4,494 \times 10^6$ lb) (0.065) (0.0001) = 26,900, say 27,000 lb

Low = (0.92) ($4,494 \times 10^6$ lb) (0.065) (0.000001) = 269 lb

6. Atrazine, propazine, and simazine: In response to a written inquiry (see Appendix B), Ciba-Geigy Corporation, the sole producer of these products, reported that HCB is contained in the products and in the waste material. Geigy also reports that:

1. The total HCB leaving their plant in liquid, gaseous, and solid waste streams is 15.4 lb/day.

2. The total HCB leaving the plant as impurities in products is 0.006 lb/day.

3. No HCBD is formed in these production operations.

Assume 300 operating days per year. Then, the total HCB emitted is:

300 x 15.406 = 4,622 lb HCB/year

Assume 4,622 to be the low value for operations with the high value equal to 4,622 x 2 or 9,244 lb HCB per year.

7. Pentachloronitrobenzene: The estimated U.S. production of pentachloronitrobenzene (PCNB) in 1972 was 3 million pounds.

PCNB is reported[5/] to be contaminated with HCB, but no specific information concerning the extent of contamination in this product could be ascertained.

On the basis of data reported in the industry for similar pesticide products (e.g., Dacthal®, atrazine, etc.), assume a high HCB contamination of 0.2% and a low of 0.1%, and that no HCBD is formed.

Then, HCB formed is:

High = (3,000,000) (0.002) = 6,000 lb HCB

Low = (3,000,000) (0.001) = 3,000 lb HCB

8. Mirex: Estimated U.S. production for 1972 is ≤ 1 million pounds.

An EPA representative has indicated[5/] that this pesticide is contaminated with HCB. No evidence was obtained that HCBD is formed.

On the basis of data reported in the industry for similar pesticides, assume a high HCB contamination of 0.2% and a low of 0.1% in Mirex. Then, estimated HCB formed is:

High = (1,000,000) (0.002) = 2,000 lb

Low = (1,000,000) (0.001) = 1,000 lb

9. Other chemical industries: No evidence was found that a significant environmental contamination by HCB or HCBD could occur in the following industries. Therefore, these industries were not included in these estimates.

- Hexachlorobenzene;
- Hexachlorobutadiene;
- Sodium chlorate;
- Pentachlorophenol;
- Pentachlorobenzene (very limited production for marketing ≤ 1 ton/year);
- Hexachloroethane;
- Synthetic rubber;
- Maleic hydrazide;
- Chlorinated naphthalene;
- Chlorinated biphenyl; and
- Hexachlorocyclopentadiene.

VII. WASTE DISPOSAL

The generation and characterization of process wastes which may contain HCB and/or HCBD are described in Section IV for each of the 23 chemicals investigated. The following discussion deals with waste treatment and disposal practices currently used for these waste materials, a general description of waste disposal technology used for chlorinated hydrocarbon products, and an estimate of the potential for HCB and HCBD contamination of industrial wastes, by-products and products.

During the course of these studies, an unsuccessful attempt was made to determine the breakdown of the various corporate waste disposal methods (i.e., percentages using incineration, landfill or deep-well injection) used in each of the chemical industries of interest. MRI inquiries (e.g., telephone and written communications) failed to develop the required data to support this type of analysis. Some companies failed to respond because such waste disposal information was considered to be proprietary; other companies, which did not supply this requested information, gave no reasons for their refusal to respond.

The waste disposal operations described in this section are separated into two categories:

A. Waste Disposal for Chemical Processes Known to Produce HCB and/or HCBD

B. Waste Disposal for Chemical Processes with Theoretical, But Not Proven, Production of HCB and/or HCBD

A. Waste Disposal for Chemical Processes Known to Produce HCB and/or HCBD

1. Hexachlorobenzene: The Stauffer Chemical Company, the only domestic producer of this chemical in 1974, has indicated that at their Louisville, Kentucky, facility, HCB is recovered for sale from a by-product tar formed during production of perchloroethylene. The remainder of this tar is reported to be recycled to the process (see Table III, p. 74).

2. Hexachlorobutadiene: This chemical is not currently produced in the U.S., and therefore, there are no domestic waste disposal operations for this industry.

3. Chlorine: The "heavy ends" waste from purification (distillation) of liquified chlorine contain chlorinated hydrocarbons and possibly some HCB and HCBD. This waste is generally disposed of by sanitary landfill or high temperature incineration.

The technical literature indicates that the estimated destruction efficiency of high temperature incineration units is almost 100%, and that the estimated installation time required for chlorinated hydrocarbon wasteburners in the chlorine industry is about 2 years.[7]

4. Carbon tetrachloride: The procedures for waste disposal generally include incineration or landfill.

Vulcan Materials Company at their carbon tetrachloride plants in Wichita, Kansas, and Geismar, Louisiana, dispose of these "hex residues" (solids containing HCB and HCBD) by impounding the waste within the plant sites in an earth-covered groundfill.[16]

Dow Chemical Company disposes of its carbon tetrachloride production wastes at Freeport, Texas, Plaquimine, Louisiana, and Pittsburg, California, by on-site incineration. Dow reports that the incineration operating conditions are proprietary and that the incineration effectiveness is excellent (99.9+% destruction).[15]

5. Perchloroethylene: Industry disposal practices for the tarry residues (hex wastes) produced in production of perchloroethylene include on-site or off-site incineration, deep-well disposal and landfill as shown in Table III, p. 74.

The Diamond Shamrock Chemical Company (Deer Park, Texas) packages its "hex" residues, which contain HCBD and HCB, in sealed containers and ships them to a private waste disposal organization (Rollins International, Inc., Houston, Texas) for incineration.[20] Exhaust gases from incineration are scrubbed with sodium hydroxide solution; the scrubbing solution is discharged to the environment without further treatment (see Appendix B).

At Plaquemine, Louisiana, Dow Chemical Company incinerates their "hex" waste from their perchloroethylene operations. Dow reports[15] that for their perchloroethylene plants at Freeport, Texas, and at Pittsburg, California, plans are under way to install similar type incinerators (see Appendix B).

The Vulcan Materials Company plants in Wichita, Kansas, and Geismar, Louisiana, produce "hex" residues containing HCBD and HCB contaminants. These residues are impounded within the plant sites in an earth-covered groundfill (see Appendix B).

In 1973, an Ethyl Corporation spokesman reported[21] that the "hex" residues from their perchloroethylene-trichloroethylene production operations (containing about 67% HCBD and 1% HCB) were disposed of in a deep well (8,000 ft deep).

PPG Industries, Inc., at Lake Charles, Louisiana, was scheduled to have a waste incinerator in operation by July 1973 to dispose of "hex" wastes from perchloroethylene production operations. Prior to that date, the wastes were landfilled.

Representatives at the Louisville, Kentucky, perchloroethylene plant, operated by Stauffer Chemical Company, have reported that the by-product contains about 80% HCB and 10% HCBD. The HCB is recovered for sale, and the remainder of the by-product is recycled to the process.

6. Trichloroethylene: The waste disposal methods conducted in this industry, as shown in Table III, p. 74, are similar to those used for perchloroethylene processes. Incineration appears to be the preferred method for waste disposal. In 1973, one facility disposed of trichloroethylene process wastes by deep-well injection, another facility used landfill operations, and a third shipped all of its waste to an off-site treatment plant (operated by an independent contractor) for disposal by incineration.

7. Dacthal®: The only domestic Dacthal® manufacturing facility, located at Greens Bayou, Texas, ships the liquid waste (containing 84% HCB and no HCBD) in sealed containers to an independent company site (Rollins, International, Deer Park, Texas) for final disposal by incineration. Documentation for this disposal method is given in the results of a written inquiry (see Appendix B).

8. Atrazine: The still bottoms, consisting of reject heavy residue liquid containing 2,000 ppm by weight of HCB and no HCBD are shipped to an independent processor for final disposal by incineration. The vent scrubber emissions, consisting of a vapor containing only 0.024 ppm of HCB and no HCBD is vented to the atmosphere. These data were obtained from a written inquiry (see Appendix B).

9. Propazine and simazine: These chemicals are produced domestically in the same single facility used for atrazine production and the wastes involved also contain HCB. The process wastes from manufacture of propazine and simazine are disposed of by the methods used for atrazine (see Appendix B).

10. Pentachlorobenzene: No information was obtained concerning disposal of waste materials from production of pentachlorobenzene as a captive by-product. It is probable that the disposal methods are similar to those used for other chlorinated wastes, e.g., incineration.

11. Pentachloronitrobenzene: Our inquiries to producers failed to develop any specific disposal information for this chemical production process.

12. Mirex: MRI inquiries to industry spokesmen did not develop any specific information concerning waste disposal practices used in the production of this pesticide.

B. Waste Disposal for Chemical Processes with Theoretical, But Not Proven, Production of HCB and/or HCBD

1. Sodium chlorate: Waste control techniques vary considerably as indicated in the following description of methods provided by Hooker Chemical Company and Pennwalt Corporation.[12]

Hooker Chemical Company's plant, at Columbus, Mississippi, reported that carbon from the electrodes is lost at a rate of 15 lb/ton of $NaClO_3$ produced. Approximately 12 lb of carbon is recovered to be sold. Most of the remaining 3 lb ends up in the "mud" waste stream of the process.

Plant emissions consist primarily of the "mud" and gaseous effluents. The mud consists of the bottoms of the cells and the settling and filtration systems following the addition of $BaCl_2$ to the cells' liquor. The most important mud constituents are barium chromate, barium sulfate, and graphite from the electrodes. This mud is discharged into the river nearby. Hooker plans to start landfilling this "mud" by 1975.

Gaseous emissions come from the cells in the form of hydrogen, CO_2 (less than 1% of hydrogen) and traces of chlorine. They are vented directly to the atmosphere. Hooker is not aware of any chlorinated hydrocarbons being formed in the cells.

Pennwalt apparently does not have the same kind of mud disposal problem as other chlorate producers. They treat the brine prior to electrolysis with sodium carbonate in order to precipitate most of the magnesium and calcium. This precipitated material, also called "mud," is presently allowed to accumulate at the Pennwalt chlorate plant. Evidently, they have plenty of space and this disposal technique is acceptable.

2. Sodium metal: The waste disposal methods for the sodium metal industry are similar to those used in the chlorine industry.

3. Vinyl chloride monomer: The major wastes of interest to this study are the "heavy ends" from fractionation steps. Because of the high cracking temperature, it is possible that significant amounts of HCB are formed as by-products in the process and concentrated in the "heavy ends" (waste material). Industry spokesmen from Dow Chemical Company and Ethyl Corporation have reported that HCBD is not generated in this industry.[15,21]

Waste disposal is accomplished by methods similar to those used in the perchloroethylene industry. Incineration is reported by the industry to be a principal method of waste disposal.

4. Pentachlorophenol: Little information is available from the literature and industrial sources pertaining to disposal of pentachlorophenol waste streams. No specific data on waste-disposal practices were obtained.

5. Hexachloroethane: Sodium chloride solution which is the only major waste, is disposed of by deep-well injection or through controlled dilution to streams.

6. Synthetic rubber: Waste disposal information for the chloroprene manufacturing industry was obtained from one company spokesman.[22] A sizable quantity of solid waste is produced during chloroprene production. This waste consists largely (90%) of reject rubber in the form of "coagulum," a nondegradable, insoluble, and nonflammable material which is disposed of by landfill operations at the Du Pont chloroprene facility. Du Pont has a chemical waste incinerator at its facility, which it uses to dispose of certain liquid chlorinated hydrocarbon wastes formed in chloroprene processing. Hydrogen chloride formed in the waste-burning operation is absorbed by scrubbing with water and the hydrochloric acid solution formed is then injected into a deep well operated by Du Pont. Du Pont has reported[22] that no HCB or HCBD is contained in any of these wastes.

7. Maleic hydrazide: No specific data were obtained pertaining to waste disposal in this industry.

8. Hexachlorocyclopentadiene: Waste disposal methods used in hexachlorocyclopentadiene (HCP) manufacture are shown in Table V. The Hooker Chemical Corporation incinerates HCP plant wastes at the Niagara Falls, New York, site.[23] The Velsicol Chemical Corporation incinerates plant wastes at the Memphis, Tennessee, site and uses deep-well injection for waste disposal at Marshall, Illinois.[24]

9. Chlorinated naphthalenes: The Koppers Company, Inc., is the only domestic producer of these chemicals. The inert distillation residue, which is produced in small quantities during the Koppers Company process operations, is hauled to a plant landfill. This residue has not been analyzed for toxic substances, but a company pollution abatement officer has indicated that he does not believe that this disposed waste creates any pollution problems or health hazards involving HCB or HCBD.[25]

The Koppers Company process uses liquid separators, absorbers, packed columns, total condensers, and a wet scrubber to prevent atmospheric emissions. The company has reported that stack testing by an ASTM method showed that no hydrogen chloride (HCl) or chlorine (Cl_2) was present. Based on the detection limits for this testing, the emission is reported to be less than 3 ppm by volume of HCl and less than 0.2 ppm by volume of Cl_2. On a weight basis, the total emission is less than 0.01 lb/hr.[26]

TABLE V

WASTE DISPOSAL METHODS USED IN HEXACHLOROCYCLOPENTADIENE MANUFACTURE[23,24]

Manufacturer	Location	Waste Disposal Method
Hooker Chemical Corporation	Montague, Michigan	Shipped by tank car to Niagara Falls, New York, and incinerated.
	Niagara Falls, New York	Incineration
Velsicol Chemical Corporation	Memphis, Tennessee	Incineration
	Marshall, Illinois (captive HCP production)	Deep well injection

10. Chlorinated biphenyls: The Monsanto Company is the only domestic producer. In Monsanto's waste disposal operation, scrap liquids containing chlorinated biphenyls are incinerated at about 2700°F for a 1.5 sec retention period and the off-gases are scrubbed to remove hydrogen chloride. This extremely high incineration temperature damages the incinerator refractory and necessitates above average repair work (e.g., about three times the normal frequency of repairs to refractories). However, Monsanto considers this damage a reasonable sacrifice to ensure total destruction of PCBs and prevent environmental pollution.[27]

C. Waste Disposal Technology

A review of the technical literature served to identify some waste disposal technology[28] which may have application, directly or indirectly, to some of the waste problems which exist for the chemical processes investigated in this study. This information is also useful in characterizing the type of treatment methods and waste disposal techniques now being used in the petrochemical industry which produces many types of chlorinated hydrocarbon products. This information is presented in Tables VI, VII, and VIII.

The waste treating processes being used for selected petrochemical wastes are indicated in Table VIII. The polychloroethane wastes and ethylene dichloride are incinerated. Sodium chloride wastes are sent to deep wells or disposed of by controlled dilution to streams and bays.

Incineration of chlorinated hydrocarbons is generally carried out at about 1300°F with a residence time of approximately 1/4 sec. High energy scrubbers are used to remove HCl. A caustic or lime solution is used to partially neutralize HCl.[29]

There are several types of incinerators:

* Liquid incinerators - require the feed material to be in the liquid form.

* Rotary kiln type - particularly suited if the material to be disposed of is collected in combustible fiber drums or if material is viscous.

* Tray-type incinerators - well suited for solids. Material falls from one tray to another until there is almost complete combustion.

* Fluidized sand bed incinerators - HCB and HCBD are viscous liquids at ambient temperatures and are usually incinerated in rotary kilns or fluidized bed incinerators.

TABLE VI

HAZARDOUS MATERIALS EXPECTED IN WASTE STREAMS OF SELECTED CHEMICAL PRODUCERS AND USERS

Waste Source Description	Description of Hazardous Compounds	General Quantification Factors	Units	Annual Production for Total U.S.
Alkalies and Chlorine Industry	Cell Process Waste			
	. Calcium oxide	0.8 lb/ton of down cell Cl_2		N.A.
	. Sodium carbonate	2 lb/ton of down cell Cl_2		N.A.
	. Chlorinated hydrocarbons	1 lb/ton	1,000 lb	10,000
	. Purification mud	50 lb/ton	1,000,000 lb	500
. Vinyl Resins	Raw Water	1.5 gal/lb product	1,000,000 gal.	4,500
	. Phenols	--		
	. Carbon tetrachloride	--		
	. Chloroform	--		
Cyclic Intermediates Industrial Organic Chemicals				
. Phenol Production	. Benzene	--		
	Process Waste	--		
	. Polychloride benzene	--		
	. Tar	--		
	Chlorination of Benzene Process	670 gal/1,000 product	1,000 gal.	90,000
	. Organic chloride	50 lb/1,000 lb product	1,000 lb	7,000
. Ethylene via Pyrolysis	Raw Waste	--		
	. Organic chlorides	0.02 lb/1,000 lb product	1,000 lb	300
. Acetaldehyde via Ethylene Oxidation	Acetaldehyde Still Bottoms	--		
	. Organic chlorides	46 lb/1,000 lb product	1,000 lb	76,000
	. Organic chloride	0.16 lb/1,000 lb product	1,000 lb	800
. Methanol via Carbon Monoxide Systems	Raw Waste			
	. Organic chlorides	0.18 lb/1,000 lb product	1,000 lb	1,200
. Ethylene Dichloride via Oxy-Chlorination of Ethylene	Raw Waste	320 gal/1,000 lb product	1,000,000 gal.	2,400
	. Organic chlorides	32 lb/1,000 lb product	1,000 gal.	24,300
Acrylics	Raw Waste	0.13 gal/lb product	1,000 gal.	25,700

Source: Adapted from information contained in Reference 28.

TABLE VII

WASTE STREAMS AND TREATMENT PROCEDURES FOR SELECTED CHEMICALS

Waste Media	Type Waste	Typical Pretreatment	General Treatment	Disposal Media	Collectable Residue	General Quantification Factors	Potential Hazard	Fully Treated On-Site	Discharged to Sewer
Cyclic Intermediates - SIC-2815 Industrial Organic Chemicals - SIC-2818									
Water									
(The wastes listed are examples of typical waste streams)	Chlorinated hydrocarbon wastes	Distillation	Neutralization	Water	Spent analysts solids	$> 1 \times 10^8$ lb/year	Chlorinated hydrocarbons		
	Polymerization wastes	Distillation	Neutralization lagooning	Landfill	Slimes	$> 1 \times 10^8$ lb/year	Phosphates		
	Ethylene oxide wastes	--	Neutralization	Water	No	Unknown	Organic chemicals		
Air	Hydrocarbons	--	Scrubbers filters	Landfill	Filter cakes scrubber solids	> 2% of volatile products--estimated as 10×10^9 lb/year	Air pollutant	Unknown	No
Product	Residuals of all organic chemicals packed and shipped	--	Municipal landfill incineration	Landfill air	Yes No	< 1-2% of total production (120×10^9 lb)	Toxic, flammable explosive chemicals None	Unknown	Unknown
Industrial Inorganic Chemicals - SIC-2819									
Air									
Hydrochloric acid (2 million tons/year)	Chlorination waste gases	Recycling	Recovery Absorbers Scrubbers	Air	No	0.1-0.3% loss	Air pollutant		
Chlorine (9 million tons/year)	Waste gases	--	Scrubbers Absorbers By-product production	Air	No	1-2% loss	Acute reaction		

Source: Adapted from information contained in Reference 28.

TABLE VIII

WASTE TREATING PROCESSES BEING USED FOR SELECTED PETROCHEMICAL WASTES

	Physical Treatment								Chemical Treatment			Biological Treatment			Ultimate Disposal						
Wastes from Petrochemical Operations	Sedimentation	Filtration	Flotation	Separators (API)	Stripping	Adsorption and Extraction	Evaporation	Submerged Combustion	pH Adjustment	Chemical Oxidation	Coagulation and Chemical Precipitation	Biological Filters	Activated Sludge	Lagoons	Controlled Dilution to Streams and Bays	At Sea	On Land Surfaces	Dumping or Burial	Deep Wells	Incineration	Salvage
Allyl chloride																				X	
Carbon tetrachloride																					X
Chlorinated hydrocarbons												X				X			X	X	X
Chloroform																				X	X
Dichloropropane																				X	
Ethyl chloride																				X	
Ethylene dichloride																				X	
Ethylidene chloride																					
Epichlorohydrin																				X	
Methyl chloride															X				X	X	X
Methylene chloride																					
Polychloroethane																				X	
Propylene dichloride																				X	
Sodium chloride															X				X		
Chlorine					X									X	X						
Waste caustic sodas										X					X				X	X	X
Synthetic rubber				X											X					X	

Source: Adapted from information contained in Reference 28.

In all cases, the exhaust gases from the incinerators have to be scrubbed in high energy scrubbers with caustic soda or lime solutions to neutralize HCl and other acids to salts.

D. The Potential for HCB and HCBD Contamination of Industrial Wastes, By-Products and Products

On the basis of the best available technical information collected, estimates were prepared to quantify the probable extent of HCB and HCBD formation which occurs in products, by-products and waste materials during normal operation of chemical industries of interest to this study.

The results of this study serve to identify the major and minor industries in respect to possible HCB and HCBD contamination of the environment and to indicate the appropriate priorities for the scheduled EPA monitoring of suspect industries in a separate program following the completion of Task I. These Estimates were made for those industries, in the field of 23, which appeared to have a substantial potential for the generation of HCB or HCBD.

The supporting assumptions and calculations made in this study are shown in Section IV, Part C, along with a brief description of the probable contaminated materials (e.g., products, by-products or waste streams). The results of this study are presented in Tables IX and X.

The estimates in Table IX show that three related chemical industries, carbon tetrachloride, perchloroethylene, and trichloroethylene account for about 89% of the HCB and more than 99% of the HCBD.

For the chemical processes considered in Table IX, the total generated HCB was estimated to be in the range of 2.4 to 4.9 million pounds in 1972. The estimated total HCBD ranged from 7.3 million to 14.5 million pounds.

Table X shows the estimated quantities of HCB and HCBD generated per ton of product. These data can be conveniently used to obtain an estimate of the HCB and HCBD generated at any individual chemical production site.

TABLE IX

ESTIMATED TOTAL QUANTITIES OF HCB AND HCBD PRESENT IN INDUSTRIAL WASTES, BY-PRODUCTS AND PRODUCTS IN 1972

Product	U.S. Production in 1972 (000 lb)	HCB (000 lb)[a/] High	HCB (000 lb)[a/] Low	HCBD (000 lb)[a/] High	HCBD (000 lb)[a/] Low
Perchloroethylene	734,800	3,500	1,750	8,670	4,340
Trichloroethylene	427,000	450	230	3,000	1,500
Carbon Tetrachloride	997,000	400	200	2,790	1,400
Chlorine	19,076,000	390	160	70	40
Dacthal®	2,000	100	80	0	0
Vinyl Chloride	4,494,000	27[b/]	0	0	0
Atrazine, Propazine, Simazine	112,000	9	5	0	0
Pentachloronitrobenzene	3,000	6	3	0	0
Mirex	1,000	2	1	0	0
		4,884	2,429	14,530	7,280

[a/] Rounded to nearest 10,000 lb--except for vinyl chloride, atrazine, propazine, simazine, pentachloronitrobenzene, and mirex.

[b/] Preliminary estimate--see Section IV-C.

TABLE X

ESTIMATED QUANTITIES OF HCB AND HCBD GENERATED PER TON OF PRODUCT IN 1972[a]

Product	U.S. Production in 1972 Short Tons	HCB (lb/ton of product)		HCBD (lb/ton of product)	
		High	Low	High	Low
Perchloroethylene	367,400	9.5	4.8	23.6	11.8
Trichloroethylene	213,500	2.1	1.1	14.1	7.1
Carbon Tetrachloride	498,500	0.8	0.4	5.6	2.8
Chlorine	9,538,000	0.04	0.02	0.007	0.004
Dacthal®	1,000	100.00	80.00	0.0	0.0
Vinyl Chloride	2,545,000	0.01	-	0.0	0.0
Atrazine, Propazine, Simazine	56,000	0.16	0.09	0.0	0.0
Pentachloronitrobenzene	1,500	4.0	2.0	0.0	0.0
Mirex	500	4.0	2.0	0.0	0.0

---

[a] See Section VI-C (p. 73) for a description of assumptions and calculations used in estimating these values.

VIII. USES FOR CHEMICAL PRODUCTS

This section provides a listing and brief discussion which outlines the major and minor uses of the 23 selected chemicals which were studied. Uses as raw materials or as intermediates in other major manufacturing processes are indicated, and other commercial applications are also noted.

To the extent possible, use patterns are presented in terms of the estimated percentage utilized for each area of application. For some chemicals, where percentage usage data could not be obtained, a general description of uses is given.

Since most of the chemical processes of interest in this study involve production of chlorine or various chlorinated hydrocarbons, MRI prepared a detailed materials flow diagram showing chlorine consumption patterns in the U.S. This diagram, presented in Figure 28, indicates the major chlorine compounds, products of special interest, production data, and use patterns for all chlorinated products.

A. Hexachlorobenzene

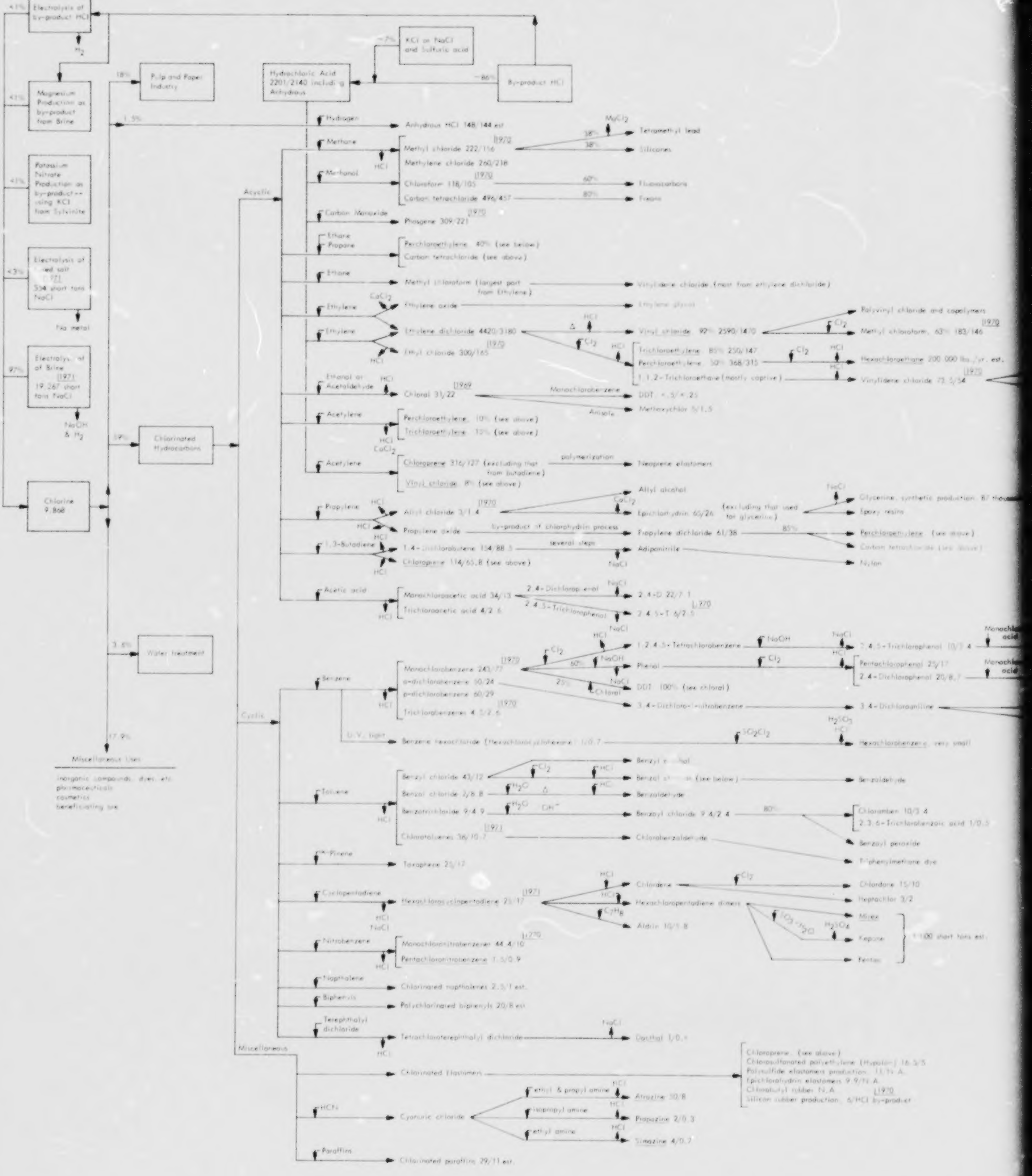
In 1972, the principle use was reported to be as a fungicide to control wheat bunt and smut fungi of other grains. The technical grade used in agriculture is reported to contain 98% hexachlorobenzene, 1.8% pentachlorobenzene, and 0.2% of 1,2,4,5-tetrachlorobenzene. Commercial formulations applied as dusts contain 10 to 40% hexachlorobenzene.[3]

Other applications in 1972 included additives for pyrotechnic compositions for the military, a porosity controller in the manufacture of electrodes, a chemical intermediate in dye manufacture and organic synthesis, and use as a wood preservative.

In 1974, a spokesman for the Stauffer Chemical Company reported that Stauffer's entire HCB production capacity (the largest in the industry) had been committed on a multi-year contract basis for use only as a rubber peptizing agent in nitroso and styrene type rubber manufacture for automobile tire plants.[30]

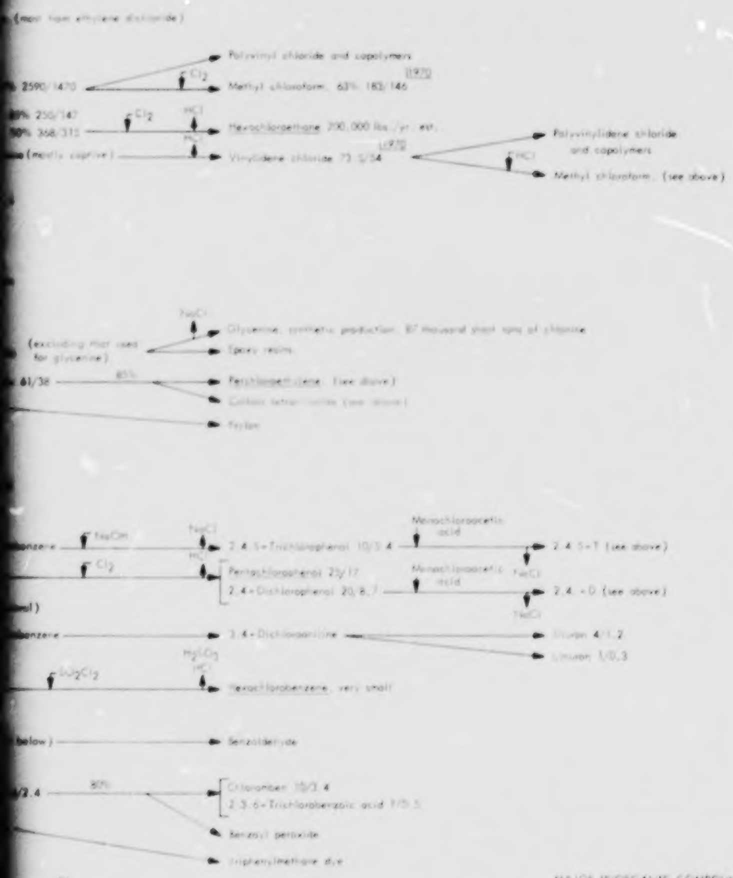
B. Hexachlorobutadiene[2,31]

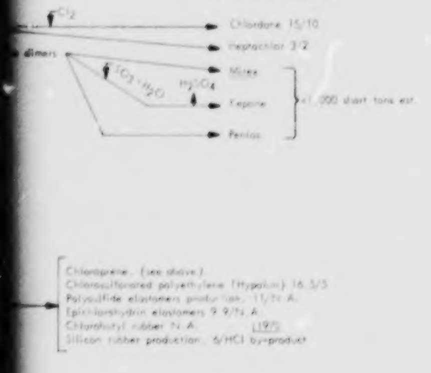
HCBD was not produced in the U.S. as of June 1974; it is imported from Germany by Dynamit Nobel America who is the only supplier of HCBD in the U.S. Approximately 200,000 to 500,000 lb of HCBD are sold annually in the U.S.

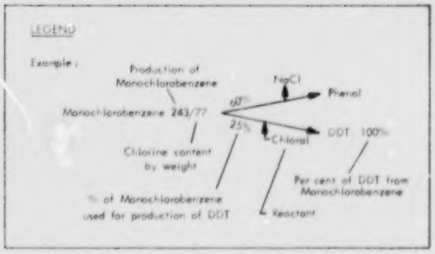


<1%
Electrolysis of by-product HCl
H_2
<1%
Magnesium Production as by-product from Brine
<1%
Potassium Nitrate Production as by-product-- using KCl from Sylvinite
<3%
Electrolysis of fused salt 1971 554 short tons NaCl
Na metal
97%
Electrolysis of of Brine 1971 19,267 short tons NaCl
NaOH & H_2
Chlorine 9,868
18%
Pulp and Paper Industry
1.5%
19%
Chlorinated Hydrocarbons
3.8%
Water treatment
17.9%
Miscellaneous Uses
inorganic compounds, dyes, etc.
pharmaceuticals
cosmetics
beneficiating ore
Hydrochloric Acid 2201/2140 including Anhydrous
~7%
KCl or NaCl and Sulfuric acid
~86%
By-product HCl
Acyclic
Hydrogen
Anhydrous HCl 148/144 est.
Methane
Methanol
HCl
Methyl chloride 222/116 1970
Methylene chloride 260/218
Chloroform 118/105 1970
Carbon tetrachloride 496/457
$MgCl_2$
38%
Tetramethyl lead
38%
Silicones
60%
Fluorocarbons
80%
Freons
Carbon Monoxide
Phosgene 309/221 1970
Ethane
Propane
Perchloroethylene 40% (see below)
Carbon tetrachloride (see above)
Ethane
Methyl chloroform (largest part from Ethylene)
Vinylidene chloride (most from ethylene dichloride)
Ethylene
$CaCl_2$
Ethylene oxide
Ethylene glycol
Ethylene
Ethylene dichloride 4420/3180
Ethyl chloride 300/165 1970
HCl
Δ
HCl
Vinyl chloride 92% 2590/1470
Polyvinyl chloride and copolymers
Cl_2
Methyl chloroform, 63% 183/146 1970
Cl_2
HCl
Trichloroethylene 85% 250/147
Perchloroethylene 50% 368/315
1,1,2-Trichloroethane (mostly captive)
Cl_2
HCl
Hexachloroethane 200,000 lbs./yr. est.
HCl
Vinylidene chloride 72.5/54 1970
Ethanol or Acetaldehyde
HCl
Chloral 31/22 1969
Monochlorobenzene
DDT <.5/<.25
Anisole
Methoxychlor 5/1.5
Acetylene
Perchloroethylene 10% (see above)
Trichloroethylene 15% (see above)
HCl
$CaCl_2$
Acetylene
Chloroprene 316/127 (excluding that from butadiene)
Vinyl chloride 8% (see above)
polymerization
Neoprene elastomers
Propylene
HCl
Allyl chloride 3/1.4 1970
HCl
Propylene oxide
Allyl alcohol
$CaCl_2$
Epichlorhydrin 65/26
(excluding that used for glycerine)
NaCl
Glycerine, synthetic production 87 thous
Epoxy resins
by-product of chlorohydrin process
Propylene dichloride 61/38
85%
Perchloroethylene (see above)
Carbon tetrachloride (see above)
HCl
1,3-Butadiene
1,4-Dichlorobutene 154/88.5
Chloroprene 114/65.8 (see above)
HCl
several steps
NaCl
Adiponitrile
Nylon
Acetic acid
Monochloroacetic acid 34/13
Trichloroacetic acid 4/2.6
HCl
2,4-Dichlorophenol
NaCl
2,4-D 22/7.1
2,4,5-Trichlorophenol
2,4,5-T 6/2.5 1970
NaCl
Cyclic
Benzene
Monochlorobenzene 243/77 1970
o-dichlorobenzene 50/24
p-dichlorobenzene 60/29
Trichlorobenzenes 4.5/2.6 1970
HCl
Cl_2
HCl
1,2,4,5-Tetrachlorobenzene
60%
NaOH
Phenol
25%
NaCl
Chloral
DDT 100% (see chloral)
3,4-Dichloro-1-nitrobenzene
NaOH
NaCl
2,4,5-Trichlorophenol 10/3.4
Cl_2
HCl
Pentachlorophenol 25/17
2,4-Dichlorophenol 20/8.7
Monochlo acid
Monochlo acid
3,4-Dichloroaniline
U.V. light
Benzene hexachloride (Hexachlorocyclohexane) 1/0.7
SO_2Cl_2
H_2SO_3
HCl
Hexachlorobenzene, very small
Toluene
Benzyl chloride 43/12
Benzal chloride 2/8.8
Benzotrichloride 9/4.9
Chlorotoluenes 36/10.7 1971
HCl
Cl_2
HCl
H_2O
Δ
HCl
H_2O
OH^-
Benzyl alcohol
Benzal chloride (see below)
Benzaldehyde
Benzoyl chloride 9.4/2.4
Chlorobenzaldehyde
Benzaldehyde
80%
Chloramben 10/3.4
2,3,6-Trichlorobenzoic acid 1/0.5
Benzoyl peroxide
Triphenylmethane dye
α-Pinene
Toxaphene 25/17
Cyclopentadiene
Hexachlorocyclopentadiene 25/17 1971
HCl
NaCl
HCl
Chlordene
HCl
Hexachloropentadiene dimers
C_7H_8
Aldrin 10/5.8
Cl_2
Chlordane 15/10
Heptachlor 3/2
SO_3
H_2O
H_2SO_4
Mirex
Kepone
Pentac
1,100 short tons est.
Nitrobenzene
Monochloronitrobenzenes 44.4/10 1970
Pentachloronitrobenzene 1.5/0.9
HCl
Napthalene
Chlorinated napthalenes 2.5/1 est.
Biphenyls
Polychlorinated biphenyls 20/8 est.
Terephthalyl dichloride
Tetrachloroterephthalyl dichloride
HCl
NaCl
Dacthal 1/0.4
Miscellaneous
Chlorinated Elastomers
Chloroprene (see above)
Chlorosulfonated polyethylene (Hypalon) 16.5/5
Polysulfide elastomers production N.A.
Epichlorohydrin elastomers 9.9/N.A.
Chlorobutyl rubber N.A.
Silicon rubber production 6/HCl by-product 1970
HCN
Cyanuric chloride
ethyl & propyl amine
HCl
Atrazine 50/8
isopropyl amine
HCl
Propazine 2/0.3
ethyl amine
HCl
Simazine 4/0.7
Paraffins
Chlorinated paraffins 29/11 est.

Figure 28 - Chlorine Consumption Pattern (major chlorine compounds and compounds of special interest)


(most from ethylene dichloride)
2590/1470
Polyvinyl chloride and copolymers
Cl_2
1970
Methyl chloroform, 63% 183/146
250/147
368/315
Cl_2
HCl
Hexachloroethane 200,000 lbs./yr. est.
HCl
(mostly captive)
1970
Vinylidene chloride 73.5/54
Polyvinylidene chloride and copolymers
HCl
Methyl chloroform. (see above)
NaCl
(excluding that used for glycerine)
Glycerine, synthetic production: 87 thousand short tons of chlorine
Epoxy resins
61/38
85%
Perchloroethylene. (see above)
Carbon tetrachloride (see above)
Nylon
NaOH
NaCl
2,4,5-Trichlorophenol 10/3.4
Monochloroacetic acid
2,4,5-T (see above)
NaCl
Cl_2
HCl
Pentachlorophenol 25/17
2,4-Dichlorophenol 20/8.7
Monochloroacetic acid
2,4,-D (see above)
NaCl
3,4-Dichloroaniline
Diuron 4/1.2
Linuron 1/0.3
H_2SO_3
HCl
SO_2Cl_2
Hexachlorobenzene, very small
below)
Benzaldehyde
/2.4
80%
Chloramben 10/3.4
2,3,6-Trichlorobenzoic acid 7/5.5
Benzoyl peroxide
Triphenylmethane dye


Cl_2
Chlordane 15/10
Heptachlor 3/2
dimers
Mirex
SO_3+H_2O
H_2SO_4
Kepone
Pentac
<1,000 short tons est.
Chloroprene. (see above)
Chlorosulfonated polyethylene (Hypalon) 16.5/5
Polysulfide elastomers production, 11/N.A.
Epichlorohydrin elastomers 9.9/N.A.
Chlorobutyl rubber N.A.
1970
Silicon rubber production, 6/HCl by-product


LEGEND
Example:
Production of Monochlorobenzene
Monochlorobenzene 243/77
60%
25%
NaCl
Phenol
Chloral
DDT, 100%
Chlorine content by weight
Per cent of DDT from Monochlorobenzene
% of Monochlorobenzene used for production of DDT
Reactant

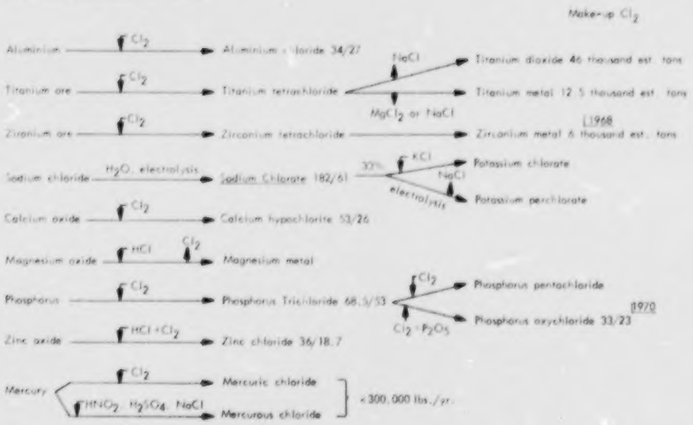
NOTES

1972 U.S. Production figures unless otherwise noted.
All weights in thousands of short tons/year.
N.A. - Not available.
Underlined compounds are of special interest to task 1.
Major Production Figure Sources
    Synthetic Organic Chemicals, 1970, U.S. Tariff Commission.
    Chemical and Engineering News, June 4, 1973.
    Predicasts, 1973, Predicasts, Inc.
    Chemical Economics Handbook, Stanford Research Institute, 1972.
    Chemical Marketing Reporter.

MAJOR BY-PRODUCTS

Hexachlorobutadiene, not isolated or marketed
Pentachlorobenzene, not isolated or marketed
Hexachlorobenzene 0.3/0.2

MAJOR INORGANIC COMPOUNDS


Make-up Cl_2
Aluminium
Cl_2
Aluminium chloride 34/27
NaCl
Titanium dioxide 46 thousand est. tons
Titanium ore
Cl_2
Titanium tetrachloride
Titanium metal 12.5 thousand est. tons
$MgCl_2$ or NaCl
1968
Zirconium ore
Cl_2
Zirconium tetrachloride
Zirconium metal 6 thousand est. tons
Sodium chloride
H_2O, electrolysis
Sodium Chlorate 182/61
30%
KCl
Potassium chlorate
NaCl
electrolysis
Potassium perchlorate
Calcium oxide
Cl_2
Calcium hypochlorite 53/26
Magnesium oxide
HCl
Cl_2
Magnesium metal
Phosphorus
Cl_2
Phosphorus Trichloride 68.5/53
Cl_2
Phosphorus pentachloride
1970
Phosphorus oxychloride 33/23
$Cl_2+P_2O_5$
Zinc oxide
$HCl+Cl_2$
Zinc chloride 36/18.7
Mercury
Cl_2
Mercuric chloride
HNO_3, H_2SO_4, NaCl
Mercurous chloride
<300,000 lbs./yr.

The largest domestic use of HCBD is for recovery of "snift" (chlorine-containing) gas in chlorine plants. This "snift" gas, which occurs at the liquification unit, is cleaned by passing it through HCBD or carbon tetrachloride. Many chlorine producers have changed to the use of HCBD in recent years. Dow Chemical Company is a major consumer of HCBD for this purpose.

The Halocarbon Company, a firm manufacturing high-temperature lubricants, has used HCBD as a fluid for gyroscopes and as a chemical intermediate to produce lubricants. Halocarbon now uses very little HCBD because of the decline in aerospace business.

HCBD is also used as a chemical intermediate in the manufacture of rubber compounds. Mallinckrodt Chemical Works at Raleigh, North Carolina, is a major user of HCBD for this application.

The technical literature indicates that HCBD has been used in Russia as a fumigant to treat grape phylloxera. Industry sources indicate that Russia is one of the major HCBD-consuming countries and uses 600 to 800 metric tons per year. Most of this material is routed to herbicidal use, primarily for grape phylloxera in the Ukraine.

C. Chlorine[4/]

The percentage distribution of major chlorine uses is shown below.

	Percent of Total Use
1. Manufacture of Chlorinated Hydrocarbons	59
2. Pulp and Paper Manufacturing	18
3. Water Treatment	4
4. Miscellaneous	19
	100

D. Sodium Chlorate[4,12/]

	Percent of Total Use
1. Pulp Bleaching	85-90
2. Herbicide and Defoliant	5
3. Other Chlorates and Perchlorates	5
4. Miscellaneous	0-5
	100

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E. Sodium Metal[4/]

Metallic sodium is primarily used in the manufacture of tetraethyl and tetramethyl lead. Minor uses include reduction of metal halides to the metals (e.g., titanium tetrachloride to titanium metal).

F. Carbon Tetrachloride[4/]

	Percent of Total Use
1. Fluorocarbons	85
2. Grain Fumigants	8
3. Solvents	5
4. Miscellaneous (includes use as reaction intermediate for other organic compounds)	2
	100

G. Perchloroethylene[4/]

	Percent of Total Use
1. Textile Industry	58
2. Exports	17
3. Metal Cleaning	15
4. Chemical Intermediate	9
5. Miscellaneous	1
	100

H. Trichloroethylene[4/]

	Percent of Total Use
1. Metal Degreasing	87
2. Extraction Solvent (e.g., drycleaning)	3
3. Miscellaneous Uses	2
4. Exports	8
	100

Miscellaneous applications include use as a low-temperature heat transfer medium and as a component of various rust-prevention formulations.

I. Vinyl Chloride Monomer[4]

Vinyl chloride is a starting material for production of polyvinyl chloride and its copolymers, and for methyl chloroform.

J. Pentachlorophenol[12]

		Percent of Total Use
1.	Wood Preservative (penta)	78
2.	Manufacture of Sodium Pentachlorophenolate	17
3.	Home and Garden Applications	3
4.	Herbicide	2
		100

K. Pentachlorobenzene

This chemical is produced largely as a captive intermediate for the synthesis of specialty chemicals. The total domestic sales in 1972 are estimated to be less than 1 ton.[15]

L. Hexachloroethane[4]

This product is used in a wide variety of applications; these uses are listed below.

1. As an additive in smoke-producing mixtures. This is one of the principle applications.

2. A mixture of hexachloroethane and sodium silicofluoride (20% by weight) has been patented for use in degassing magnesium.

3. As an additive for extreme pressure lubricants.

4. To reduce ignitability of combustible liquids.

5. Fungicidal and insecticidal components.

6. Veterinary medicine--used for treatment of liver flukes of cattle and sheep.

7. Moth repellent.

8. Plasticizer for cellulose esters.

9. As rubber vulcanizing accelerator.

10. Retardant in fermentation processes.

11. Component of submarine paints.

12. Fire-extinguishing fluids additive.

M. Synthetic Rubber (chloroprene)[4]

Chloroprene is used primarily in polymerization processes for the production of neoprene elastomers.

N. Atrazine[12]

Atrazine is a selective herbicide. The major use is on corn and some is used on sorghum. Very little is used by industry (less than 10%).

O. Propazine

Propazine is a preemergence herbicide used for control of broad-leaved and grassy weeds in millet, sorghum, and umbelliferrous crops.

P. Simazine[12]

Simazine is a widely used selective herbicide for control of broadleaf and grassy weeds in corn, citrus, deciduous fruits and nuts, established alfalfa, perennial grasses, and nursery plantings. It is also used as a nonselective herbicide for vegetation control in noncropland.

Q. Pentachloronitrobenzene (PCNB)[4]

Pentachloronitrobenzene is used as a soil fungicide to control diseases of cotton, potatoes, tomatoes and peppers. Use of 20% PCNB in dust also gives satisfactory results as a seed disinfectant against smut.

R. Dacthal®[12]

Dacthal® is a preemergence herbicide used for cotton, peanuts, and a variety of vegetables.

S. Mirex[12]

Mirex is used for the control of some species of ants, and most widely in the USDA's fire ant program in the southeastern states. It has also been used for the control of cotton pests, and some Hawaiian pineapple growers have used it for control of mealy bugs and ants. It is generally used as a bait now.

T. Maleic Hydrazide[4]

This product is used as a herbicide and plant growth inhibitor. For example, it is used to control suckering of tobacco and for sprout control on potatoes and onions. Another application involves the treatment of turf or lawns to limit the number of mowings required. It may be used to delay the flowering of fruit trees or the growth of shrubbery and nursery plants until frost danger is past. It is marketed in the form of the sodium or diethanolamine salts; the former contains 50% of the hydrazide and the latter 30%.

U. Hexachlorocyclopentadiene (HCP)[4]

	Percent of Total Use
1. Chlorendic Anhydride	28
2. Chlordane	33
3. Other Pesticides	39
	100

Chlorendic anhydride is an intermediate for the production of flame-retardant plasticizers, fire-resistant polyester resins and paints, and as a dye intermediate. HCP is a key intermediate in the manufacture of the cyclodiene group of chlorinated insecticides. For example, HCP is the starting material for the preparation of an estimated 45 to 50 million pounds per year of pesticides including mirex, dieldrin, endrin, aldrin, chlordane, heptachlor, and others.

V. Chlorinated Naphthalenes[26]

The major uses for chlorinated naphthalenes are as a dielectric for electronic components, as an additive in gear oils and cutting oils, and as a flame-resistant component of plastics.

W. Chlorinated Biphenyls[4,13,14]

Polychlorinated biphenyls (PCBs) have been used in the U.S. and elsewhere over the past 40 years for many industrial and consumer applications.

Prior to 1971, about 40% of PCB products sold in the U.S. was used in applications where containment was difficult and losses into the environment were probable. These uses included plasticizers, hydraulic fluids and lubricants, surface coatings, inks, adhesives, pesticide extenders and encapsulated dyes for carbonless duplicating paper. The remaining 60% of domestic sales was used primarily in electrical applications (transformers and capacitors).

During the period of 1969 to 1971, scientific evidence was accumulated which indicated that the PCBs were widely dispersed throughout the environment and that they can have adverse ecological and toxicological effects. PCBs which enter the environment can be stored in animal lipids. These biphenyls resist metabolic changes and tend to be concentrated at succeedingly higher levels in animals higher in the food chain. The identification of PCBs as a potential food contaminant was first reported in 1966. Subsequent investigations established several sources from which foods may become contaminated with PCBs. The acute toxicities of PCBs in animals is reported to be low. Alterations in the functioning of the liver have been observed in a number of animal species and these alterations are attributed to PCBs.[13,14]

Because of these developments, the Monsanto Company undertook certain voluntary restrictions in 1971 on the distribution of PCBs to various industries. Under these restrictions, PCBs were sold only for electrical applications in which the PCB is confined inside sealed containers. In 1971, this type of electrical application represented 90% of the total use.

IX. ENVIRONMENTAL AND HEALTH ASPECTS

This section describes and briefly discusses the environmental and health aspects of the production of the two chemicals of primary interest, HCB and HCBD, and also of the three related chemicals first identified as of special interest to this study, i.e., pentachlorophenol, hexachloroethane, and pentachlorobenzene. The information includes data taken from Chemical Abstracts and miscellaneous technical publications. The following outline describes the toxic hazard ratings used:

Toxic Hazard Rating Code[32/]

0 NONE: (a) No harm under any conditions; (b) harmful only under unusual conditions or overwhelming dosage.

1 SLIGHT: Causes readily reversible changes which disappear after end of exposure.

2 MODERATE: May involve both irreversible and reversible changes, not severe enough to cause death or permanent injury.

3 HIGH: May cause death or permanent injury after very short exposure to small quantities.

U UNKNOWN: No information on humans considered valid by authors.

A. Hexachlorobenzene

General Information[32/]

Synonym: Perchlorobenzene

Description: Monoclinic prisms

Formula: C_6Cl_6

Constants: Mol wt: 284.80; m.p.: 230°C; b.p.: 326°C; flash p.: 242°F; d: 1.5; vap. press.: 1.089 x 10^{-5} mm Hg at 20°C, 1 mm Hg at 114.4°C; vap. d.: 9.8

HCB is a very stable, unreactive compound. It is not hydrolized in aqueous solutions and there is no evidence that it is broken down by physical or chemical processes in the environment. Since HCB is volatile in water vapor even at low temperatures, co-distillation is a mechanism for dispersal. HCB sublimes readily and will evaporate if exposed to air under conditions of adequate ventilation. The literature[3] indicates that aerial dispersion may be the major pathway for HCB entering the marine environment.

The results of model ecosystem studies conducted at the University of Illinois on the environmental fate of hexachlorobenzene and five other organochlorine pesticides (aldrin, dieldrin, endrin, mirex, and DDT) were reported in 1973.[33] A summary of these reported results is given in the following paragraphs.

The basic model ecosystem methodology utilized radiotracer techniques. The model ecosystem evaluation was conducted in a small glass aquarium with a terrestrial-aquatic interface of pure sand. A measured portion of radiolabeled pesticide was applied to sorghum seedlings grown on the terrestrial portion. Salt-marsh caterpillars were fed on the leaves and their fecal products and the larvae themselves contaminated the aquatic portion of the system. The radiolabeled products were transferred through several food chains, e.g., alga, snail, plankton, water flea, mosquito, and fish. After 33 days in an environmental plant growth chamber at 80°F and a 12-hr photo period, the experiment was terminated, and the amount and nature of the ^{14}C determined by homogenization of the organisms, extraction with acetonitrile, TLC autoradiography, and liquid scintillation counting. Wherever possible, identity of degradation products was determined by chromatography with known standards. The results for hexachlorobenzene and its degradation products expressed as equivalent ppm values are shown in Table XI.

TABLE XI

DISTRIBUTION OF HEXACHLOROBENZENE AND DEGRADATION PRODUCTS

	Hexachlorobenzene Equivalents (ppm)					
	H_2O	Alga (oedogonium)	Snail (physa)	Mosquito (culex)	Water flea (daphnia)	Fish (gambusia)
Total ^{14}C	0.00644	1.827	4.099	0.737	0.696	3.154
Hexachlorobenzene (R_f = 0.80)[a/]	0.00298	1.556	3.72	0.429	0.598	0.857
Pentachlorophenol (R_f = 0.50)	0.00034	--	--	--	--	--
Unknown I (R_f = 0.10)	0.00023	--	--	--	--	0.446
Unknown II (R_f = 0.05)	--	--	--	--	--	0.857
Polar (R_f = 0.0)	0.00143	0.271	0.378	0.269	0.098	0.995
Unextractable	0.00197	--	--	--	--	--

[a/] TLC with benzene:acetone, 1:1.

Source: Adapted from information contained in Reference 33.

Hexachlorobenzene was found in substantial quantities in the various organisms with little evidence of degradation products except highly polar materials and conjugates. Hexachlorobenzene comprised 85.1% of the total radioactivity in alga, 90.8% in the snail, 87.2% in the water flea, 58.3% in the mosquito, and 27.2% in the fish. The water phase contained an appreciable quantity of pentachlorophenol. This compound was not found in free form in any of the organisms of the system. Hydrolysis of polar products in the water showed a family of related compounds which are other chlorinated phenols. The reported information indicates that another investigator has tenatively identified 2,4,5-trichlorophenol, along with pentachlorophenol, as urinary degradation products of hexachlorobenzene in the rat.

The biodegradability index (BI) values for hexachlorobenzene were 0.46 in fish and 0.10 in snail, and ecological magnification values (EM) were 287 in fish and 1,247 in snail as shown in Table XII.

TABLE XII

QUANTITATIVE VALUES FOR ECOLOGICAL MAGNIFICATION (EM) AND BIODEGRADABILITY INDEX (BI) FOR EIGHT ORGANOCHLORINE PESTICIDES IN FISH AND SNAIL

	H_2O Solubility (ppm)	Fish (gambusia)		Snail (physa)	
		EM	BI	EM	BI
Hexachlorobenzene	0.006	287	0.46	1,247	0.10
Aldrin					
As Aldrin	0.20	3,140	0.00014	44,600	0.0017
As Dieldrin		5,957	0.00013	11,149	0.00016
Dieldrin	0.25	2,700	0.0018	61,657	0.0009
Endrin	0.23	1,335	0.009	49,218	0.0124
Mirex	0.085	219	0.0145	1,165	0.006
Lindane	7.3	560	0.091	456	0.052
DDT	0.0012	84,545	0.015	34,545	0.044
DDE	0.0013	27,358	0.032	19,329	0.017
DDD or TDE	ca. 0.002	83,500	0.054	8,250	0.024

Source: Adapted from information contained in Reference 33.

These data show that hexachlorobenzene accumulated in the tissues of fish and snail to levels much greater than that in the water of the model systems.

Toxicity

The results of a hazard rating for HCB reported in the technical literature[32] are presented below.

Toxic Hazard Rating

Acute Local: Irritant 1

Acute Systemic: Ingestion 1

Chronic Local: Irritant 1

Chronic Systemic: U

Toxicology: Limited animal experiments suggest low toxicity

Fire Hazard: Slight, when exposed to heat or flame

Disaster Hazard: Dangerous, when heated to decomposition, it emits highly toxic fumes of chlorides

Other pertinent findings in the toxicological literature on HCB are summarized in the following paragraphs.

There are few data (see Table XIII) on the single dose acute toxicity of HCB. For single dose administration, HCB has a very low toxicity--500 mg/kg interperitoneal is nonlethal in rats, and the oral lethal dose of a 15% suspension of HCB in the female Japanese quail is greater than 1 g/kg.[3] On the other hand, the subacute or chronic toxicity of HCB can be significant, as shown in Table XIV.[3] The most pronounced effect of chronic exposure appears to be dysfunction of the liver. Neurotoxic symptoms were observed in several of these studies.

F. DeMarteis[34] and co-workers have reported on the nervous and biochemical disturbances resulting from oral administration of HCB to rats and other test animals. R. K. Ockner and R. Schmid[35,36] have reported on acquired porphyria in man and rat caused by HCB intoxications. H. Ehrlicher[37] has discussed industrial observations of the toxicity of vaporous HCB; he reports that no serious illnesses or changes of liver function in the blood compound were noted by medical monitoring of production workers exposed to HCB vapors over a 40-year period. Finally, in a review by I. V. Sairtskii,[38] it was found that an HCB concentration of 0.1 mg/liter could be assumed to represent the threshold toxicity value, and that 1/100 of that value may then represent the limit of permissible concentration of HCB in air for workers.

TABLE XIII

ACUTE TOXICITY OF HEXACHLOROBENZENE FOLLOWING SINGLE DOSE ADMINISTRATION

Species	Method of Administration	Minimum Toxic Dose	Average Lethal Dose (ppm)	Total Lethal Dose
Mice	Oral	400	4,000	7,500
Rats	Oral	500	3,500	6,000
Rabbits	Oral		2,600	
Cats	Oral		1,700	
Guinea Pigs	Oral		> 1,000	
Guinea Pigs	Oral		> 3,000	
Guinea Pigs	Oral		3,000	
Bluegill Fish	Water		> 100	
Flathead Minnows	Water		> 100	
Rainbow Trout	Water		> 100	
Channel Carfish	Water		> 100	
Rats	Interperitoneal		> 500	

Source: Adapted from information contained in Reference 3.

TABLE XIV

SUBACUTE AND CHRONIC TOXICITY OF HEXACHLOROBENZENE

Route	Species	Number of Animals	Dose	Test Duration	Effects Observed
Oral (in feed)	Rats	5	2 mg/kg/day	13 days	No toxic effects.
		5	6 mg/kg/day	13 days	Very light skin twitching and nervousness. Significant incorporation into liver.
		5	20 mg/kg/day	13 days	Neurotoxic symptoms. Increase in liver weight.
		5	60 mg/kg/day	13 days	Neurotoxic symptoms. Increase in liver and kidney weight.
		5	200 mg/kg/day	13 days	Neurotoxic symptoms. Increase in liver and kidney weight.
Oral (in feed)	Rats	4	10 mg/kg/day	30 days	No toxic effects.
Oral (in feed)	Rats	4	30 mg/kg/day	30 days	Increase in food consumption and body weight gains, increase in coproporphyrin excretion in urine; liver weight and liver: body weight ratio increased.
		4	65 mg/kg/day	30 days	Same as at 30 mg/kg/day.
		4	100 mg/kg/day	30 days	Same as 30 mg/kg/day plus elevation in excretion of uroporphyrim.

TABLE XIV (Continued)

Route	Species	Number of Animals	Dose	Test Duration	Effects Observed
Oral (in feed)	Rats	33	100 mg/kg/day	51 days	13 deaths in 1 month; neurotoxic symptoms; increased liver weight; porphyria.
Oral (in feed)	Rats	10	300 mg/kg/day	10 days	30% mortality.
		10	150 mg/kg/day	30 days	60% mortality.
		10	50 mg/kg/day	30 days	30% mortality.
Oral (in water)	Rats	13	0.025 mg/kg/day	4-8 months	No toxic symptoms. Possible effect on conditioned reflexes.
Oral (in feed)	Japanese Quail	15	1 ppm	90 days	No toxic effects.
		15	5 ppm	90 days	Slight increase in liver weight; minimal porphyria.
		15	20 ppm	90 days	Increased liver weight, decreased egg production; porphyria; liver and kidney pathological changes.
		15	80 ppm	90 days	5 deaths (18- to 62-day period); neurotoxic symptoms; porphyria; increased liver weight; decreased egg production and hatchability; liver and kidney pathological changes.

TABLE XIV (Concluded)

Route	Species	Number of Animals	Dose	Test Duration	Effects Observed
Oral (in feed)	Japanese Quail	12	2,500 ppm	30 days	All died in 30 days. (4 died in 7 days).
		12	500 ppm	30 days	All died within a month.
		12	100 ppm	3 months	Mortality (1-20th day; 10 within 7 weeks; 1-10 weeks). Surviving cock showed marked loss of weight. Necrosis of liver cells; porphyria.
Oral (in feed)	Chickens		120-480 ppm in diet	3 months	No toxic effects.
Oral (in feed)	Guinea Pig		0.5%	8-10 days	Marked neurological symptoms.
	Mice		0.5%	8-10 days	Marked neurological symptoms.
Oral (in feed)	Rabbits		0.5%	6 weeks	Increase in urinary porphyrins.
			0.5%	8-12 weeks	Death occurred.
Oral (in feed)	Male Rats	26	0.2%	12 weeks	Retardation in weight gain; porphyria; degenerative changes in the liver.

Source: Adapted from information contained in Reference 3.

B. Hexachlorobutadiene

General Information[39]

Formula: C_4Cl_6

Constants: Mol wt: 260.7; melting range: -19 to 22°C; boiling range: 210 to 220°C; d: 1.675; vap. press.: 1.5 mm Hg at 40°C

Toxicity

HCBD toxicity tests conducted by the Hazelton Laboratories of Washington, D.C., for the Diamond Shamrock Corporation[29] are discussed in the following paragraphs.

The acute oral LD_{50} of HCBD for male albino rats is 178 μl/kg of body weight. At a dosage level of 100 μl/kg none of a group of five animals succumbed. At a level of 316 μl/kg, all of a group of five animals succumbed within 2 days.

The acute dermal LD_{50} of HCBD for albino rabbits of either sex is 1,780 μl/kg of body weight. After an exposure period of 24-hr none of a group of four rabbits succumbed at a dosage level of 1,000 μl/kg. At a dosage level of 3,160 μl/kg, all of a group of five rabbits succumbed within a period of 5 days. The exposed skins of all animals showed a mild to moderate degree of erythema. This completely subsided by the second or third day and thereafter showed no gross signs of dermal irritation.

A single application of 0.05 HCBD to the eyes of a group of three albino rabbits of either sex produced a mild degree of eye irritation which completely subsided within 24 hr. There was no evidence of systemic toxicity from mucous membrane absorption.

The acute inhalatic Lt_{50} for varying species is:

	Lt_{50} - (min)	95% Confidence Limits - (min)
Mice	310	270 to 357
Rats	275	229 to 330
Guinea Pigs	200	165 to 242

Ten mice, 10 rats, and 10 guinea pigs were exposed for 6 hr to the aerosol of HCBD under dynamic conditions in a chamber. Normal concentration of the compound in the experimental atmosphere was 6,800 ppm (72,750 mg/m^3). Direct comparison between compounds from the above data are only permissible if the concentration in each case were the same. However, a rough comparison of the toxicities of two other compounds, trichlorofluoroethylene (TCFE), and perchloroethylene (PCE), can be made, if it is assumed that the same quantitative response of the organism may be expected for various values of C and t, provided (Ct) is a constant. The $L(Ct)_{50}$ for these three compounds is given below:

Compound	Mean Concentration Of Available Data (ppm)	Mean Concentration Of Available Data (mg/m^3)	$L(Ct)_{50} \times 10^{-6}$ (mg-min/m^3) Mice	Rats	Guinea Pigs	Average
HCBD	6,800	72,750	22.6	20.00	14.6	19.1
PCE	2,750	18,600	9.0	10.00	16.0	11.7
TCFE	4,120	25,100	23.0	36.00	39.0	32.6

Other pertinent findings in the technical literature on HCBD toxicity are summarized in the following paragraphs.

In 1967, V. F. Chernokan[40/] observed in skin intake toxicity studies, that HCBD caused skin irritation and hypermia in rats, with extreme toxicological effects at concentrations approaching the LD_{50} of 4.33 g/kg (165 mg/kg, oral). At 3.0 to 3.5 g/kg the animals displayed increased motibility and agression, followed by paralysis of the extremities.

John C. Gage[41/] conducted a study in 1970 of the subacute toxicity of 109 industrial chemicals. He found major kidney damage in rats exposed for periods of about 3 weeks to known concentrations of HCBD. The results indicated degeneration of the protein, fat, and carbohydrate relations in cells and impared cell function.

Stroganov and Kolosova[42/] found that HCBD is toxic to some aquatic organisms (e.g., Daphnia magma, Leucaspius delineatus, and fish) at concentrations of 3 mg/liter of water.

F. G. Murzakaev[43/] conducted toxicity studies in which rats were fed 20 mg/kg doses of HCBD. The results indicated degeneration of the protein, fat, and carbohydrate relations in cells and impared cell function.

C. Pentachlorophenol

General Information[32/]

Description: Dark-colored flakes and sublimed needle crystals with a characteristic odor

Formula: Cl_5C_6OH

Constants: Mol wt: 266.4; mp: 191°C; b.p.: 310°C (decomposes); d: 1.978; vap. press.: 40 mm at 211.2°C

The results of a hazard ratings for this chemical reported in the technical literature[32/] are shown below.

Toxic Hazard Rating

Acute Local: Irritant 3, Ingestion 3, Inhalation 3

Acute Systemic: Ingestion 3, Inhalation 3, Skin Absorption 3

Chronic Local: Irritant 2

Chronic Systemic: Ingestion 2, Inhalation 2, Skin Absorption 2

Toxicology: Acute poisoning is marked by weakness, convulsions, and collapse. Chronic exposure can cause liver and kidney injury.

Disaster Hazard: Dangerous, when heated to decomposition it emits highly toxic fumes of chlorides.

D. Hexachloroethane

General Information[32/]

Synonyms: Carbon trichloride; carbon hexachloride

Description: Rohmbic, triclinic or cubic crystals, colorless; camphor-like odor

Formula: CCl_3CCl_3

Constants: Mol wt: 236.76; m.p.: 186.6°C (sublimes); d: 2.091; vap. press.: 1 mm at 32.7°C

The result of hazard ratings reported in the technical literature[33/] are given below.

Toxic Hazard Rating[32/]

Acute Local: Irritant 2, Ingestion 2, Inhalation 2

Acute Systemic: Inhalation 2

Chronic Local: Irritant 2

Chronic Systemic: Ingestion 2

Toxicology: Liver injury has been described from exposure to this material.

Explosion Hazard: Slight, by spontaneous chemical reaction. Dehalogenation of this material by reaction with alkalies, metals, etc., will produce spontaneously explosive chloroacetylenes.

Disaster Hazard: Dangerous, when heated to decomposition, it emits highly toxic fumes of phosgene.

E. Pentachlorobenzene[32/]

Toxicology: Very little data concerning toxic properties of this chemical are available in the technical literature. The literature[32/] indicates that the toxicity of this product is usually no greater, and frequently is less than that of corresponding aromatic hydrocarbons.

Fire Hazard: Unknown

Explosion Hazard: Unknown

Disaster Hazard: Moderately dangerous, when heated to decomposition, toxic fumes may be emitted.

X. SELECTION OF MONITORING SITES

An important objective in this study was to identify those chemical plant sites that appear to be most likely to produce significant amounts of HCB and HCBD as by-products, wastes, etc., and therefore pose a potential threat of environmental contamination. Criteria were therefore developed and then applied to all of the pertinent chemicals and processes to select those specific plant sites which should be tested for HCB and HCBD emissions in a subsequent EPA program.

The major selection criteria developed and applied by MRI in this evaluation were:

* Total volumes of production of chemicals at each plant site.

* Total volume of discharge of waste materials of all types (liquids, solids, and gases). Emphasis is placed on volume of liquids and solids since HCB and HCBD have low volatility and, therefore, tend to collect in these types of waste.

* The known application of advanced pollution control technology--e.g., the degree of sophistication of waste treatment and waste disposal method in use at specific plant sites.

* The age of manufacturing plants and facilities and the known process improvements which minimize pollution.

* The toxicity of the product(s) being produced.

* Production of captive products of interest used on the plant site as an intermediate, etc., as opposed to production for marketing.

* The reputation of companies or specific plants for high standards of safety and/or pollution control in production operations.

To the extent possible, these criteria were applied to each of the identified chemical industries of interest to Task I. In some instances, as noted, the available collected information for a given industry was insufficient to support an evaluation of this type. The principal task involved narrowing the field of plant sites in the chlorine industries because of the large number of chlorine plants (65) and the wide geographic distribution of these plants. A detailed discussion of the evaluation methodology for the chlorine plants and other industries is presented in Appendix C.

A brief discussion of the evaluation methods and results for each of the chemical industries of interest is given below under subheadings.

Chlorine plants: In 1973 there were 65 chlorine producing plants in the U.S. Twenty-nine plants used diaphragm cells, 23 plants employed mercury cells, and 13 plants used miscellaneous cell types or combinations of cells. The 32 plants which use dimensionally stable anodes (DSAs) do not form HCB or HCBD. The other 33 (nonDSAs) plants are considered to be potential emitters of both of these chemicals.

Following application of the MRI criteria to the 33 nonDSA chlorine plants (see Appendix C), the field was narrowed to the plant sites shown in Table XV.

TABLE XV

CHLORINE PLANTS RECOMMENDED AS MONITORING TEST SITES

Type Plant	Plant Site	Producer
Diaphragm cell	1. Houston, Texas	Champion International Corporation
	2. Gramercy, Louisiana	Kaiser Aluminum and Chemical Corporation
Mercury cell	3. Linden, New Jersey	Linden Chlorine Products, Inc.
	4. McIntosh, Alabama	Olin Corporation

It is suggested that initial monitoring tests be made only at Sites (2) and (4). If these tests show substantial HCB and HCBD contamination problems then it is recommended that follow-up testing be conducted at Sites (1) and (3).

Sodium chlorate plants: This chemical industry is not considered to be a source of HCB and HCBD contamination. No evidence of such contamination was obtained by inquiries made to producers of this chemical. All domestic sodium chlorate producers are in the process of converting from graphite electrodes to the more efficient metallized anodes (DSAs). The use of these new electrodes eliminates the formation of chlorinated hydrocarbon wastes resulting from the deterioration of the graphite electrode.

Carbon tetrachloride plants: As of 1973, carbon tetrachloride was produced at 11 plant sites. The evaluation results (see Appendix C) are a recommendation that the following carbon tetrachloride plant sites be monitored:

- E. I. du Pont de Nemours, Corpus Christi, Texas
- Vulcan Materials Company, Geismar, Louisiana
- Vulcan Materials Company, Wichita, Kansas

Perchloroethylene plants: Perchloroethylene was produced at 10 production sites in 1973. The results of the MRI evaluation (see Appendix C) indicate that the following perchloroethylene plants should be recommended as monitoring test sites:

- PPG Industry, Inc., Lake Charles, Louisiana
- Vulcan Materials Company, Geismar, Louisiana
- Vulcan Materials Company, Wichita, Kansas

Trichloroethylene plants: Trichloroethylene was produced at five plant sites in 1973. Each of these plants is operated in conjunction with perchloroethylene operations at a common site. The results of the MRI evaluation warrant that the trichloroethylene plant of PPG Industry, Inc., at Lake Charles, Louisiana, be recommended as a monitoring site.

Vinyl chloride monomer plants: In 1973, very large quantities ($5,089 \times 10^6$ lb/year) of vinyl chloride monomer were being produced in the United States. The total number of operating plant sites during that year was 16. On the basis of the MRI evaluation (see Appendix C) one representative vinyl chloride monomer plant was selected for inclusion in the list of recommended monitoring test sites. The recommended site is the Lake Charles, Louisiana, facility of PPG Industry, Inc.

Pentachlorophenol plants: Information on the technology of this chemical industry indicates that the potential for environmental contamination by HCB or HCBD is very low or nonexistent. The Dow Chemical Company claims no HCB is formed in their pentachlorophenol process and Monsanto also reports that it has no problem with the formation of HCB in its pentachlorophenol production operations. For these reasons, no monitoring test site is recommended.

Hexachlorobenzene plants: Based on information obtained in Task I, this chemical is produced largely as a by-product of the manufacture of other chemicals such as perchloroethylene, etc. The actual processes used are proprietary. The Stauffer Chemical Company, the only domestic producer of HCB in 1974, produces a by-product HCB in their perchloroethylene (PCE) manufacturing operations at Louisville, Kentucky. The tarry residue from PCE operations is reported by an industry spokesman to contain about 80% HCB and 10 HCBD. The HCB is recovered and sold and the remainder of the tar is recycled to the process reactor. Therefore, the possibility of HCB or HCBD entering the environment is considered to be very slight. This plant is, therefore, not recommended for inclusion in the EPA site monitoring program.

Pentachlorobenzene: An industry spokesman[15/] has reported that this chemical is produced largely as a captive by-product (e.g., it is used as an intermediate or disposed as waste on the plant site), by the manufacturers of tetrachlorobenzene who are as follows:

Dover Chemical Corporation, Dover Ohio
Dow Chemical Company, USA, Midland, Michigan
Hooker Chemical Corporation, subsidiary of
  Occidental Petroleum Corporation, Niagara Falls, New York
Solvent Chemical Company, Inc., Malden, Massachusetts

Two specialty chemical companies are reported to produce and sell pentachlorobenzene in very small quantities (i.e., less than 2,000 lb/year) for both companies. These companies are: Aceto Chemical Company, Inc., of Flushing, New York, and Chemical Procurement Labs, Inc., of College Point, New York. The estimated total domestic production in 1972 was 1,000 to 2,000 tons. Since some HCB is formed as a by-product in the production process, there is some risk of HCB pollution. Because this chemical is produced principally as a captive product, which is consumed or disposed of on the plant site, it is not recommended that any of these production sites be included in the EPA site monitoring program.

Hexachloroethane: This chemical is manufactured domestically by only one producer, Hummel Chemical Company, at South Plainfield, New Jersey. In 1972, the production amounted to only 200 tons, which combined with the low process operating temperature (100 to 140°C), makes it very unlikely that this process poses any problem in regard to HCB or HCBD contamination. Therefore, this production plant is not recommended for inclusion in the list of EPA monitoring sites.

Hexachlorobutadiene: Within recent years (i.e., during the 1960's) HCBD was produced and sold as a by-product of the manufacture of perchloroethylene and trichloroethylene. In 1974, however, no HCBD was produced domestically and all U.S. supplies, amounting to 200,000 to 500,000 lb, were obtained by imports from Dynamit Nobel in Germany. Thus, it is not appropriate to consider site monitoring of HCBD plants in the U.S.

Synthetic rubber (chloroprene): In 1974, chloroprene (the only synthetic rubber deemed of interest to Task I) was being produced at six manufacturing sites in the U.S. The total domestic production capacity in 1974 was 198,000 tons. Waste disposal information for the chloroprene manufacturing process was obtained from a Du Pont spokesman.[22] A sizable quantity of solid waste consisting largely (90%) of reject rubber in the form of "coagulum," a nondegradable, insoluble and nonflammable material, is disposed of by landfill operations at the Du Pont facility. Du Pont incinerates certain liquid chlorinated hydrocarbon wastes formed in chloroprene processing. The hydrogen chloride produced in the waste-burning operation is absorbed by water scrubbing and the hydrochloric acid solution formed is then injected into a deep well operated by Du Pont. This spokesman reported that neither HCB nor HCBD are present in the wastes from this industry. Because this spokesman's report concerned over two-thirds of the total chloroprene production, no chloroprene plants are recommended for monitoring.

Atrazine, propazine, and simazine: Ciba-Geigy Corporation produces all of these pesticide products at its St. Gabriel, Louisiana, facility. This plant is designed primarily for atrazine, but is used also for the other two triazines. MRI studies show that significant quantities of HCB can be formed in the manufacture of this group of pesticides. On the basis of these studies, it is recommended that the St. Gabriel, Louisiana, facility of Ciba-Geigy be included in the group of plant sites for test monitoring.

Pentachloronitrobenzene (PCNB): The chemical is produced domestically solely by the Olin Corporation at McIntosh, Alabama. The total 1972 production amounted to about 1,500 tons. Because HCB can be formed as a by-product in the manufacture of PCNB, it is recommended that this plant be included in the EPA site monitoring program. (It should be noted that McIntosh, Alabama, is also the location of a mercury cell chlorine plant, which has been recommended for site monitoring.)

Dacthal®: This pesticide is produced only by Diamond Shamrock Corporation at Greens Bayou, Texas. The total production in 1972 was estimated to be 1,000 tons. In response to a written inquiry, this corporation reported that the product now contains 0.3% by weight of HCB as a contaminant and that the production waste material contains about 84% HCB. All of the waste material is drummed or transferred to tank trucks and hauled to Rollins International, Inc., Deer Park, Texas, for incineration. Because production of Dacthal® increased from about 1,000 to 2,000 tons from 1972 to 1974, and the concentration of HCB in the waste is near 84%, this plant site is recommended for inclusion in the EPA site monitoring program.

Mirex: This pesticide is produced at only one site (Niagara Falls, New York, Hooker Chemical Corporation). The total annual production is estimated to be less than 500 tons. MRI has estimated relatively small quantities of HCB (from 1,000 to 2,000 lb/year) are formed in the production of mirex. Because this chemical is produced in very small quantities and at only one site, this plant is not recommended for the initial EPA site monitoring program. It is recommended, however, that representative samples of mirex products be obtained, and analyzed for HCB content to establish the extent of contamination. If substantial contamination is established, then it is recommended that the mirex production site be monitored.

Maleic hydrazide: In 1972, four plants produced a total of 2,000 tons of this chemical. No evidence was found in the Task I study to establish that any HCB or HCBD pollution problems are involved in the manufacture of this chemical. Because of the low production, and the lack of evidence concerning HCB or HCBD emissions during manufacture, none of these plants are recommended for site monitoring.

Hexachlorocyclopentadiene (HCP): In 1971, four manufacturing plants accounted for an estimated total production of 25,000 tons of HCP. Some evidence was found that HCB and HCBD may be formed in the production processes used.[6] The current producers employ advanced waste disposal technology including waste incineration. None of these production plants are recommended for inclusion in the initial EPA monitoring program, but a follow-up surveillance program involving analysis of plant products is recommended.

Chlorinated naphthalene: Only one company (The Koppers Company, Inc.) produces this chemical. The total sales volume for these products in 1974 amounted to less than 2,500 tons. A relatively low reaction temperature (maximum of about 200°C) is used in production of these products. The plant is reported[25,26] to use advanced pollution control equipment to prevent atmospheric emissions. Small amounts of inert distillation residue are hauled to a plant landfill. For these reasons, this plant is not recommended as a monitoring site.

Chlorinated biphenyls (PCB): Monsanto Chemical Company, the sole domestic producer of this type of product, has production facilities at Anniston, Alabama, and Sauget, Illinois. In response to a written inquiry (see Appendix B), the Monsanto Company has reported that in their production of PCBs no detectable concentrations of HCB or HCBD occur in the products or in process waste materials, and that no by-products are produced. On the basis of this information and an analysis of the process and product usage conditions, we conclude that the current production and use of PCBs does not create any HCB or HCBD pollution problems.

In summary, the recommended plant locations and chemical operations for the initial EPA monitoring program are:

1. Lake Charles, Louisiana - perchloroethylene, trichloroethylene, and vinyl chloride monomer.

2. Geismar, Louisiana - perchloroethylene, carbon tetrachloride.

3. Gramercy, Louisiana - chlorine by diaphragm cell process.

4. Corpus Christi, Texas - carbon tetrachloride.

5. Wichita, Kansas - perchloroethylene and carbon tetrachloride.

6. McIntosh, Alabama - chlorine by mercury cell process and pentachloronitrobenzene.

7. St. Gabriel, Louisiana - atrazine, simazine, propazine.

8. Greens Bayou, Texas - Dacthal®.

APPENDIX A

PLANT CAPACITIES, PRODUCTION AND IMPORT DATA FOR SELECTED CHEMICALS

TABLE A-Ia

SUMMARY DATA FOR THE CHLOR-ALKALI INDUSTRY

1. Salt consumption for Chlor-Alkali Production (1971)

   Sodium Chloride: 19,621,000 tons

   Potassium Chloride: 282,000 tons (est)

2. Chlor-Alkali Production:

	1971 (000 tons)	1972 (000 tons)
Chlorine	9,352	9,868
Sodium hydroxide	9,667	10,266
Potassium hydroxide	198	178
Hydrogen	156 (56×10^9 scf)	161 (58×10^9 scf)

Source: Adapted from information contained in Reference 17.

TABLE A-1b

CHLOR-ALKALI PRODUCTION[17/]

Producer	Production Site	Annual Production Capacity (10^3 tons)	Remarks
Allied Chemical Corporation Industrial Chemicals Division	Acme, North Carolina Baton Rouge, Louisiana Brunswick, Georgia Moundsville, West Virginia Syracuse (Solvay), New York	594.0	Chlorine-caustic cells
Aluminum Company of America	Point Comfort, Texas	150.0	Chlorine-caustic cells
American Magesium Company	Snyder, Texas	26.0	Chlorine-caustic cells. Not operating.
BASF Wyandotte Corporation Industrial Chemicals Group	Geismar, Louisiana	300.0	Chlorine-caustic cells
	Port Edwards, Wisconsin	55.0	Chlorine-caustic cells
	Wyandotte, Michigan	120.0	Chlorine-caustic cells
Brunswick Pulp and Paper Company Brunswick Chemical Company, Subsidiary	Brunswick, Georgia	30.0	Chlorine-caustic cells
Champion International Corporation	Canton, North Carolina	18.0	Chlorine-caustic cells
	Houston, Texas	14.4	Chlorine-caustic cells
Detrex Chemical Industry, Inc.	Ashtabula, Ohio	22.0	Chlorine-caustic cells
Diamond Shamrock Corporation	Deer Park, Texas	440.0	New plant construction
Diamond Shamrock Chemical Company Electro Chemicals Division	Deer Park, Texas Delaware City, Delaware Mobile, Alabama Muscle Shoals, Alabama Painesville, Ohio	720.0	Chlorine-caustic cells
Dow Chemical Company USA	Dallesport, Washington	Unknown	New plant construction
	Freeport, Texas	1,700.0	Also magnesium cells
	Midland, Michigan Oyster Creek, Texas Pittsburg, California Plaquemine, Louisiana	1,576.0	Chlorine-caustic cells
E. I. du Pont de Nemours and Company, Inc. Electrochemicals Department	Corpus Christi, Texas	366.0	New plant construction
	Memphis, Tennessee Niagara Falls, New York	122.4	By-product of metallic sodium manufacturing

TABLE A-Ib (Continued)

Producer	Production Site	Annual Production Capacity (10^3 tons)	Remarks
Ethyl Corporation Industrial Chemicals Division	Baton Rouge, Louisiana Houston, Texas	230.4	By-product of metallic sodium manufacturing
FMC Corporation Inorganic Chemicals Division	South Charleston, West Virginia	277.2	Chlorine-caustic cells
Fort Howard Paper Company	Green Bay, Wisconsin	Unknown	
Georgia-Pacific Corporation Bellingham Division	Bellingham, Washington	48.0	Chlorine-caustic cells
	Plaquemine, Louisiana	440.0	New plant construction
The B. F. Goodrich Company B. F. Goodrich Chemical Company, Division	Calvert City, Kentucky	108.0	Chlorine-caustic cells
Hercules, Inc. Coatings and Specialty Products Department	Hopewell, Virginia	18.0	Chlorine-caustic cells
Jefferson Chemical Company, Inc.	Port Neches, Texas	54.0	Chlorine-caustic cells
Kaiser Aluminum and Chemical Corporation Kaiser Chemicals Division	Gramercy, Louisiana	160.0	Chlorine-caustic cells
Linden Chlorine Products, Inc	Linden, New Jersey	180.0	Chlorine-caustic cells
Mobay Chemical Company, Division of Baychem Corporation	Cedar Bayou, Texas	72.0	Electrolysis
Monsanto Company Monsanto Industrial Chemicals Company	Sauget, Illinois	94.0	Chlorine-caustic cells
N L Industry, Inc. H-K, Inc., Subsidiary Magnesium Division	Rowley, Utah	80.0	New plant construction
Northwest Industry, Inc. Velsicol Chemical Corporation, Subsidiary	Memphis, Tennessee	24.8	Chlorine-caustic cells
Occidental Petroleum Corporation Hooker Chemical Corporation, Subsidiary Industrial Chemicals Division	Montague, Michigan Niagara Falls, New York Tacoma, Washington Taft, Louisiana	630.0	Chlorine-caustic cells

TABLE A-Ib (Concluded)

Producer	Production Site	Annual Production Capacity (10^3 tons)	Remarks
Olin Corporation Chemicals Division	Augusta, Georgia Charleston, Tennessee McIntosh, Alabama Niagara Falls, New York	526.2	Chlorine-caustic cells
	Saltville, Virginia		
Pennwalt Corporation Chemical Division	Calvert City, Kentucky Portland, Oregon Tacoma, Washington Wyandotte, Michigan	342.0	Chlorine-caustic cells
PPG Industry, Inc. Chemical Division Industrial Chemicals Division	Guayanilla, Puerto Rico	185.0	Chlorine-caustic cells
	Barberton, Ohio Corpus Christi, Texas Lake Charles, Louisiana New Martinsville, West Virginia	1,638.0	Chlorine-caustic cells
RMI Company	Ashtabula, Ohio	Unknown	By-product of metallic sodium manufacturing
Shell Chemical Company Industrial Chemicals Division	Deer Park, Texas	135.0	Chlorine-caustic cells
Sobin Chemicals, Inc.	Niagara Falls, New York	Unknown	Chlorine-caustic cells
	Orrington, Maine	72.0	Chlorine-caustic cells
Stauffer Chemical Company Industrial Chemical Division	Henderson, Nevada Le Moyne, Alabama St. Gabriel, Louisiana	270.0	Chlorine-caustic cells
Vicksburg Chemical Company	Vicksburg, Mississippi	33.0	Oxidation of HCl via NO_2
Vulcan Materials Company Chemicals Division	Denver City, Texas	Unknown	
	Newark, New Jersey Wichita, Kansas	153.0	Chlorine-caustic cells
Weyerhaeuser Company	Longview, Washington	100.0	Chlorine-caustic cells

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Note: Several pulp and paper companies not listed are believed to have some captive production. Much of the above capacity is produced for captive use only.

Source: Adapted from information contained in Reference 17.

TABLE A-Ic

DOMESTIC CHLORINE PRODUCERS BY EPA REGION[17/]

Company	Location	Products
Region I		
Sobin Chlor-Alkali	Orrington, Maine	Cl_2, NaOH
Region II		
Hooker	Niagara Falls, New York	Cl_2, NaOH
Olin	Niagara Falls, New York	Cl_2, NaOH
DuPont	Niagara Falls, New York	Cl_2, Na metal
Hooker, Sobin	Niagara Falls, New York	Cl_2, KOH
Allied	Syracuse, New York	Cl_2, NaOH, Na_2CO_3
Vulcan	Newark, New Jersey	Cl_2, NaOH
Linden Chlorine	Linden, New Jersey	Cl_2, NaOH
Region III		
Diamond	Delaware City, Delaware	Cl_2, NaOH
Hercules	Hopewell, Virginia	Cl_2, NaOH
Allied	Moundsville, West Virginia	Cl_2, NaOH
PPG	New Martinsville, West Virginia	Cl_2, NaOH
PMC Corporation	South Charleston, West Virginia	Cl_2, NaOH
Region IV		
Goodrich	Calvert City, Kentucky	Cl_2, NaOH
Pennwalt	Calvert City, Kentucky	Cl_2, NaOH
Velsicol	Memphis, Tennessee	Cl_2, NaOH
DuPont	Memphis, Tennessee	Cl_2, Na metal
Olin	Charleston, Tennessee	Cl_2, NaOH
Vicksburg Chemical	Vicksburg, Mississippi	Cl_2
Diamond	Muscle Shoals, Alabama	Cl_2, NaOH
Olin	McIntosh, Alabama	Cl_2, NaOH
Diamond	Mobile, Alabama	Cl_2, NaOH
Stauffer	LeMoyne, Alabama	Cl_2, NaOH
Champion	Canton, North Carolina	Cl_2, NaOH
Allied	Acme, North Carolina	Cl_2, NaOH

TABLE A-1c (Continued)

Company	Location	Product
Region IV (Concluded)		
Olin	Augusta, Georgia	Cl_2, NaOH
Allied	Brunswick, Georgia	Cl_2, NaOH
Brunswick Chemical	Brunswick, Georgia	Cl_2, NaOH
Region V		
Detrex	Ashtabula, Ohio	Cl_2, NaOH
RMI Company	Ashtabula, Ohio	Cl_2, Na metal
Diamond	Painesville, Ohio	Cl_2, NaOH, Na_2CO_3
PPG	Barberton, Ohio	Cl_2, NaOH, Na_2CO_3
BASF Wyandotte	Wyandotte, Michigan	Cl_2, NaOH, Na_2CO_3
Pennwalt	Wyandotte, Michigan	Cl_2, NaOH
Dow	Midland, Michigan	Cl_2, NaOH
Hooker	Montague, Michigan	Cl_2, NaOH
Monsanto	East St. Louis, Illinois	Cl_2, NaOH
Ft. Howard Paper	Green Bay, Wisconsin	Cl_2, NaOH
BASF Wyandotte	Port Edwards, Wisconsin	Cl_2, NaOH
Region VI		
Hooker	Taft, Louisiana	Cl_2, NaOH
Kaiser Aluminum	Gramercy, Louisiana	Cl_2, NaOH
BASF Wyandotte	Geismar, Louisiana	Cl_2, NaOH
Stauffer	St. Gabriel, Louisiana	Cl_2, NaOH
Dow	Plaquemine, Louisiana	Cl_2, NaOH
Allied	Baton Rouge, Louisiana	Cl_2, NaOH
Ethyl	Baton Rouge, Louisiana	Cl_2, Na metal, Na_2CO_3
PPG	Lake Charles, Louisiana	Cl_2, NaOH
Jefferson	Port Neches, Texas	Cl_2, NaOH
Mobay	Cedar Bayou, Texas	Cl_2
Dow	Freeport, Texas	Cl_2, NaOH
Alcoa	Point Comfort, Texas	Cl_2, NaOH
PPG	Corpus Christi, Texas	Cl_2, NaOH, Na_2CO_3
Champion	Houston, Texas	Cl_2, NaOH
Diamond	Deer Park, Texas	Cl_2, NaOH
Shell	Deer Park, Texas	Cl_2, NaOH
Ethyl	Houston, Texas	Cl_2, Na metal
Vulcan	Denver City, Texas	Cl_2, NaOH

TABLE A-Ic (Concluded)

Company	Location	Product
Region VII		
Vulcan	Wichita, Kansas	Cl_2, NaOH
Region IX		
Dow	Pittsburg, California	Cl_2, NaOH
Stauffer	Henderson, Nevada	Cl_2, NaOH
Region X		
Georgia-Pacific	Billingham, Washington	Cl_2, NaOH
Hooker	Tacoma, Washington	Cl_2, NaOH
Pennwalt	Tacoma, Washington	Cl_2, NaOH
Weyerhaeuser	Longview, Washington	Cl_2, NaOH
Pennwalt	Portland, Oregon	Cl_2, NaOH

TABLE A-II

LIST OF U.S. PRODUCERS OF SELECTED CHEMICALS[44]

Producers	Production Site	EPA Region	Annual Production Capacity (10^3 tons)[a]	Remarks
Sodium Chlorate				
Brunswick Pulp and Paper Company Brunswick Chemical Company, Subsidiary	Brunswick, Georgia	IV	7	Captive product
Huron Chemicals	Butler, Alabama	IV	4	
Georgia-Pacific Corporation Bellingham Division	Bellingham, Washington	X	4	Captive product
Kerr-McGee Chemical Corporation, Subsidiary	Hamilton, Mississippi	IV	33	
	Henderson, Nevada			
Occidental Petroleum Corporation Hooker Chemical Corporation, Subsidiary Industrial Chemicals Division	Columbus, Mississippi	IV	62	
	Niagara Falls, New York	II	16	
	Taft, Louisiana	VI	45	
Pacific Engineering and Production Company of Nevada	Henderson, Nevada	IX	6	Captive product
Penn-Olin Chemical Company	Calvert City, Kentucky	IV	31	
Pennwalt Corporation, Chemical Division	Portland, Oregon	X	16	
	Wyandotte, Michigan	V	29	MRI estimate
PPG Industry, Inc. Industrial Chemical Division	Lake Charles, Louisiana	VI	15	On standby in 1973
Riegel Paper Corporation	Naheola, Alabama	IV	4	
	Riegelwood, North Carolina	IV	7	Captive product
Sodium Metal				
E. I. du Pont de Nemours and Company, Inc.	Niagara Falls, New York	II	42	Chlorine is produced as a co-product in these plants
	Memphis, Tennessee	IV	35	

TABLE A-II (Continued)

Producers	Production Site	EPA Region	Annual Production Capacity (10^3 tons)[a/]	Remarks
Sodium Metal (Concluded)				
Ethyl Corporation	Baton Rouge, Louisiana	VI	45	
	Pasadena, Texas	VI	30	
Reactive Metals, Inc.	Ashtabula, Ohio	V	37	
Carbon Tetrachloride				
Allied Chemical Corporation Specialty Chemicals Division	Moundsville, West Virginia	III	4	From CH_4
Dow Chemical Compnay	Freeport, Texas	VI	65	From CH_4
	Pittsburg, California	IX	22.5	From CH_4, C_2Cl_4 co-product
	Plaquemine, Louisiana	VI	50	C_2Cl_4 co-product
E. I. du Pont de Nemours and Company, Inc.	Corpus Christi, Texas	VI	250	C_2Cl_4 co-product
FMC Corporation Inorganic Chemicals Division	South Charleston, West Virginia	III	150	CS_2 method
Stauffer Chemical Company Industrial Chemical Division	LeMoyne, Alabama	IV	100	CS_2 method
	Louisville, Kentucky	IV	35	From CH_4, C_2Cl_4 co-product
	Niagara Falls, New York	II	75	CS_2 method
Vulcan Materials Company Chemicals Division	Geismar, Louisiana	VI	17.5	From CH_4, C_2Cl_4 co-product
	Wichita, Kansas	VII	20	From CH_4, C_2Cl_4 co-product
Perchloroethylene				
Diamond Shamrock Corporation Diamond Shamrock Chemical Company Electro Chemicals Division	Deer Park, Texas	VI	80	
Dow Chemical Company	Freeport, Texas	VI	60	
	Pittsburg, California	IX	10	
	Plaquemine, Louisiana	VI	75	
Ethyl Corporation Industrial Chemicals Division	Baton Rouge, Louisiana	VI	25	
Occidental Petroleum Corporation Hooker Chemical Corporation, Subsidiary Industrial Chemicals Division	Taft, Louisiana	VI	25	

TABLE A-II (Continued

Producers	Production Site	EPA Region	Annual Production Capacity (10^3 tons)[a/]	Remarks
Perchloroethylene (Concluded)				
PPG Industry, Inc. Industrial Chemical Division	Lake Charles, Louisiana	VI	100	
Stauffer Chemical Company Industrial Chemical Division	Louisville, Kentucky	IV	35	
Vulcan Materials Company Chemicals Division	Geismar, Louisiana	VI	75	
	Wichita, Kansas	VII	25	
Trichloroethylene				
Diamond Shamrock Chemical Company Electro Chemicals Division	Deer Park, Texas	VI	50	Ethylene as raw material
Dow Chemical, USA	Freeport, Texas	VI	75	Ethylene as raw material
Ethyl Corporation Industrial Chemical Division	Baton Rouge, Louisiana	VI	25	Ethylene as raw material
Hooker Chemical Corporation Industrial Chemicals Division	Taft, Louisiana	VI	20	Acetylene as raw material
PPG Industry, inc. Industrial Chemical Division	Lake Charles, Louisiana	VI	140	Ethylene as raw material
Vinyl Chloride Monomer				
Allied Chemical Corporation Industrial Chemicals Division	Baton Rouge, Louisiana	VI	150	Ethylene-oxychlorination process
American Chemical Corporation	Long Beach, California	IX	87.5	Ethylene-oxychlorination process
Continental Oil Company Conoco Chemicals Division	Westlake, Louisiana	VI	325	Ethylene process
Dow Chemical Company	Freeport, Texas	VI	100	Ethylene-oxychlorination process
	Oyster Creek, Texas	VI	350	Ethylene-oxychlorination process
	Plaquemine, Louisiana	VI	195	Ethylene-oxychlorination process

TABLE A-II (Continued)

Producers	Production Site	EPA Region	Annual Production Capacity $(10^3$ tons$)^{a/}$	Remarks
Vinyl Chloride Monomer (Concluded)				
Ethyl Corporation				
Industrial Chemicals Division	Baton Rouge, Louisiana	VI	150	Ethylene-oxychlorination process
	Pasadena, Texas	VI	75	Ethylene-oxychlorination process
The B. F. Goodrich Company				
B. F. Goodrich Chemical Company, Division	Calver City, Kentucky	IV	500	Ethylene-oxychlorination process
Monochem, Inc.	Geismar, Louisiana	VI	150	Acetylene process
PPG Industry, Inc.				
Industrial Chemical Division	Lake Charles, Louisiana	VI	200	Ethylene-oxychlorination
Shell Chemical Company				
Industrial Chemicals Division	Deer Park, Texas	VI	420	Ethylene process
	Norco, Louisiana	VI	350	
Tenneco, Inc.				
Tenneco Chemicals, Inc.				
Tenneco Intermediates Division	Houston, Texas	VI	112.5	Acetylene process
Union Carbide Corporation				
Chemicals and Plastics Division	Texas City, Texas	VI	75	On standby. Balanced ethylene and acetylene
Uniroyal, Inc.				
Uniroyal Chemical Division	Painesville, Ohio	V	350	MRI estimate
Pentachlorophenol				
Dow Chemical Company	Midland, Michigan	V	7.5	
Monsanto Industrial Chemical Company	Sauget, Illinois	V	13	
Reichhold Chemicals, Inc.	Tacoma, Washington	X	6	
Vulcan Materials Company				
Chemicals Division	Wichita, Kansas	VII	3.5	
Hexachlorobenzene (HCB)				
Hummel Chemical Company, Inc.	South Plainfield, New Jersey	II	0.25	Estimated capacity. Not in operation in 1974.

TABLE A-II (Continued)

Producers	Production Site	EPA Region	Annual Production Capacity (10^3 tons)[a]	Remarks
Hexachlorobenzene (HCB) (Concluded)				
Dover Chemical Corporation	Dover, Ohio	V	0.25	Not in operation in 1974.
Stauffer Chemical Company Industrial Chemical Division	Louisville, Kentucky	IV	0.50	Estimated value
Pentachlorobenzene				
Aceto Chemical Company, Inc.	Flushing, New York	II	0.001	Specialty chemical companies,
Chemical Procurement Labs, Inc.	College Point, New York	II		MRI estimate
Dover Chemical Corporation	Dover, Ohio	V		
Dow Chemical Company	Midland, Michigan	V	NA	Produced as captive by-product; None sold commercially.
Occidental Petroleum Corporation Hooker Chemical Corporation, Subsidiary Industrial Chemicals Division	Niagara Falls, New York	II	NA	
Solvent Chemical Company, Inc.	Malden, Massachusetts	I	NA	
Hexachloroethane				
Hummel Chemical Company, Inc.	South Plainfield, New Jersey	II	0.25	MRI estimate
Hexachlorobutadiene (HCBD)				
Diamond Shamrock Corporation Diamond Shamrock Chemical Company Electro Chemicals Division	Deer Park, Texas	VI	NA	HCBD is not currently produced for commercial marketing in the U.S.
Semi Works	Ashtabula, Ohio	V	--	
Ethyl Corporation	Baton Rouge, Louisiana	VI	--	
Synthetic Rubber - Chloroprene				
E. I. du Pont de Nemours and Company, Inc.[b] Elastomer Chemicals Department	Laplace, Louisiana	VI	37.5	A new plant at Victoria, Texas, was reported to be under construction in 1974.
	Louisville, Kentucky	IV	137.5	
Petro-Tex Chemical Corporation [b]	Houston, Texas	VI	22.5	

TABLE A-II (Continued)

Producers	Production Site	EPA Region	Annual Production Capacity (10^3 tons)[a]	Remarks
Atrazine				
Ciba-Geigy Corporation Geigy Agricultural Chemicals Division	McIntosh, Alabama	IV	75	Plant designed primarily for Atrazine, but can be used for other triazines. Capacity given is total for atrazine, propazine and simazine.
	St. Gabriel, Louisiana	VI		
Propazine				
Ciba-Geigy Corporation Geigy Agricultural Chemicals Division	St. Gabriel, Louisiana	IV		
Simazine				
Ciba-Geigy Corporation Geigy Agricultural Chemicals Division	St. Gabriel, Louisiana	IV		
Pentachloronitrobenzene				
Olin Corporation Chemicals Division Custom Chemicals	McIntosh, Alabama Rochester, New York	IV II	2.0	MRI estimate
Dacthal				
Diamond Shamrock Corporation Diamond Shamrock Chemical Company Biochemicals Division	Green Bayou, Texas	VI	2.5	MRI estimate
Mirex				
Occidental Petroleum Corporation Hooker Chemical Corporation, Subsidiary Industrial Chemicals Division	Niagara Falls, New York	II	0.2	MRI estimate

TABLE A-11 (Concluded)

Producers	Production Site	EPA Region	Annual Production Capacity (10^3 tons)[a]	Remarks
Maleic Hydrazide				
The Ansul Company Chemical Division	Marinette, Wisconsin	V		
Chem Formulators, Inc. Chemical Division	Nitro, West Virginia	III		
Fairmount Chemical Company, Inc.	Newark, New Jersey	II	5	MRI estimate
Uniroyal, Inc. Uniroyal Chemical Division	Geismar, Louisiana	VI		
Hexachlorocyclopentadiene				
Occidental Petroleum Corporation				
Hooker Chemical Corporation, Subsidiary	Montague, Michigan	V		Pentane chlorination
Electrochemical and Specialties Division	Niagara Falls, New York	II		Pentane chlorination
Northwest Industries, Inc.			30	MRI estimate for 1972
Velsicol Chemical Corporation, Subsidiary	Memphis, Tennessee	IV		Pentane chlorination
	Marshall, Illinois (captive use)	V		NaOCl chlorination of cyclopentadiene from naphtha
Chlorinated Naphthalenes				
Koppers Company, Inc.	Bridgeville, Pennsylvania	III	3.0	MRI estimate, process is proprietary
Chlorinated Biphenyls				
Monsanto Company	Sauget, Illinois	V	20-25	Molten biphenyl is chlorinated with gaseous chlorine in presence of iron catalyst.

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[a] NA indication, data were not available.

[b] Data from Chemical Week, September 22, 1971.

TABLE A-III

U.S. PRODUCTION AND IMPORT DATA FOR SELECTED CHEMICALS [45,46,47,48,49]

Chemical	Year	Production for all U.S. Producers (10^3 tons)	Production Capacity for all U.S. Producers (10^3 tons)	U.S. Imports (10^3 tons)	Remarks
Chlorine	1963	5,464			Source: Chlorine Institute
	1964	5,945			
	1965	6,517			
	1966	7,204			
	1967	7,680	7,765		
	1968	8,444	8,505		
	1969	9,376	-		
	1970	9,764	10,349		
	1971	9,352	10,662	35.10	Growth per year 1972-1980 estimated at +6%
	1972	9,868	-		
Sodium Chlorate	1963	124.3	157	3.92	
	1964	136.3	-	2.42	
	1965	134.3	170	2.38	
	1966	154.2	170.5	3.23	
	1967	155.5	170.5	4.48	
	1968	167.4	201.5	6.06	
	1969	187.2	214.0	11.54	
	1970	197.7	230.5	13.55	
	1971	196.6	230.5	16.25	
	1972	214	230.5	-	
	1973	230	312	25.17	MRI estimate of production rate for 1972
Sodium Metal	1971	0.075	0.095	-	
Carbon tetrachloride (CCl_4)	1968	380			
	1969	425			
	1970	465			
	1971	505			
	1972	498.5			
	1973	525	789	-	Projections indicate that total demand for CCl_4 will increase from 500,000 to 675,000 tons from 1972 to 1977
Perchloroethylene	1963	162.5		28.75	
	1964	182.9		35.00	
	1965	214.7		25.05	
	1966	231.3		33.95	
	1967	266.5		25.00	
	1968	318.3		22.15	
	1969	317.7		17.35	
	1970	353.4		20.10	
	1971	351.7		22.20	
	1972	367.4		NA	
	1973		540	22.34	Estimated consumption growth for 1972 to 1980 is + 6.5%

TABLE A-III (Continued)

Chemical	Year	Production for all U.S. Producers (10^3 tons)	Production Capacity for all U.S. Producers (10^3 tons)	U.S. Imports (10^3 tons)	Remarks
Trichloroethylene	1960	0.175		29.6	
	1962	0.180		32.5	
	1964			37.8	
	1966			59.5	
	1968			29.3	
	1971	265		4.6	
	1972	213.5			Estimated consumption growth 1972-1975 = +9.5%, 1975-1980 = +6.5%.
	1973	236	240	23.72	
Vinyl Chloride Monomer	1969		2,000		
	1970	2,000			
	1971	2,050	-		
	1972	2,544.5	2,500		
	1973	-	2,863	0.927	Estimated production growth from 1973 to 1975 is +13.5%.
	1975	2,800	3,600	-	
Pentachlorophenol (PCP)	1963	16.96			
	1964	18.45			
	1965	19.98			
	1966	21.63			
	1967	22.12			
	1968	24.30			These figures may include some double reporting of the 13 to 14 million lb of sodium pentachlorophenate made from PCP.
	1969	23.00			
	1970	23.60			
	1971	25.45			
	1972	24.5			
	1973	23.30	26	None	
	1974	28.0	34.5		
Hexachlorobenzene	1958	0.38	NA	NA	
	1959	0.36	NA	NA	
	1960	0.22	NA	NA	
	1973	0.35	0.75-1.0	None	
Pentachlorobenzene	1972	< 0.001	0.001	NA	MRI estimate of sales volume. There is also captive production.
Hexachloroethane	1972	0.2	0.25	0.077	MRI production and capacity estimates.
Hexachlorobutadiene (HCBD)	1972	None	NA	None	HCBD is not currently produced for commercial marketing.
				0.1-.25	
Synthetic Rubber, Chloroprene	1971	178	198	-	
	1972		-	-	
	1973	-	-	7.3	
Atrazine	1972	45-55	> 75	None	MRI production estimate

TABLE A-III (Concluded)

Chemical	Year	Production for all U.S. Producers (10^3 tons)	Production Capacity for All U.S. Producers (10^3 tons)	U.S. Imports (10^3 tons)	Remarks
Propazine	1972	2	-	None	
Simazine	1972	4	-	None	
Pentachloronitrobenzene	1967	-	-	0.015	
	1968	-	-	0.010	
	1969	-	-	0.066	
	1972	1.5	2.0	-	
Dacthal	1972	1	1.3	-	
	1974	2	2.5	-	MRI estimate for 1972 capacity
Mirex	1972	< 0.5	< 0.6	-	MRI estimate
Maleic Hydrazide	1967	-	-	0	
	1968	-	-	0	
	1969	-	-	0.0017	
	1972	4	5	-	MRI estimate
Hexachloro-cyclopentadiene	1971	25.0	30	-	MRI estimates
	1972	25.0	30		MRI estimates
Chlorinated Naphthalenes	1969	< 2.5	-	-	Only 1 domestic producer
	1970	< 2.5	-	-	
	1971	< 2.5	-	-	
	1972	< 2.5	-	-	
	1973	< 2.5	3.0	-	MRI estimate of capacity
Chlorinated Biphenyls	1967	37.7	48	-	Only 1 domestic producer
	1968	42.4	48	-	
	1969	38.2	48	-	
	1970	42.5	48	-	
	1971	20.2	48	-	
	1972	19.3	24	-	
	1973	20	24	-	
	1974	20	24	-	

Basis for MRI estimates shown in this appendix: Estimated values for annual production rates and for annual production capacities were prepared by MRI on the basis of information developed by one or more of the following methods.

- Estimates provided by MRI consultants or in-house advisors.
- Extrapolation of available data which apply for different operating years.
- Calculation and application of the average production rate or capacity per plant for a given chemical industry.
- Use of applicable data for a similar product and production operation.
- Use of information provided in personal communications with company spokesmen.

APPENDIX B

RESULTS OF A WRITTEN INQUIRY TO CHEMICAL MANUFACTURERS

MRI developed a five-page questionnaire for use in more intensive industrial surveys. This questionnaire requested detailed information concerning production, use, and release into the environment of HCB and HCBD in all physical forms and as a constituent of any type of processed material. Following review and approval of this questionnaire by the U.S. Environmental Protection Agency, copies of the questionnaire, accompanies by a cover letter, were mailed to nine selected chemical companies (corporate office address) as follows:

- Dow Chemical Company
- Occidental Petroleum Corporation-Hooker Chemical Corporation
- Vulcan Materials Comapny-Chemicals Division
- Stauffer Chemical Company-Industrial Chemical Division
- Diamond-Shamrock Corporation
- Ciba-Geigy Corporation
- PPG Industry, Inc.-Industrial Chemical Division
- E. I. du Pont de Nemours and Company, Inc.
- Monsanto Company

A sample copy of the entire questionnaire, including the one-page introduction, follows.

SURVEY OF INDUSTRIAL PROCESSING DATA

Midwest Research Institute is presently conducting a program for the Office of Toxic Substances of the U. S. Environmental Protection Agency under contract No. 68-01-2105. The primary purpose of this program is to collect information on production/formation, use and release into the environment of two toxic substances, namely, hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD).

In addition to industries that directly produce or use HCB and HCBD, we have identified the following chemicals as materials whose manufacture may produce small amounts of either HCB or HCBD as a by-product, waste material, or impurity in a product.

Carbon Tetrachloride
Perchloroethylene
Chlorine
Trichloroethylene
Atrazine
Propazine
Simazine
Vinyl chloride

Dacthal
Pentachloronitrobenzene
Synthetic rubber (chloroprene
Sodium chlorate
Mirex

Hexachlorocyclopentadiene
Chlorinated napthalene
Chlorinated biphenyl

The MRI study is based on available information in the literature and private communications with industry personnel, via telephone, letters and questionnaire. We have completed searching the literature and contacting some of the chemical industries by telephone and letter inquiries. In order to get a statistically reliable overview of the industrial situation on the subject, it is important that we contact as many industries as possible. The enclosed questionnaire attempts to do just this. We, therefore, solict your co-operation in filling out the questionnaire; your early response (within 6 weeks) will be sincerely appreciated.

If your department cannot supply the requested information please forward to other departments which can respond to this questionnaire. If you have any questions concerning this questionnnaire, please call Mr. Charles Mumma at (816) 561-0202 (Extension 415).

QUESTIONNAIRE PREPARED FOR
OFFICE OF TOXIC SUBSTANCES
U.S. ENVIRONMENTAL PROTECTION AGENCY

(Please fill in the details and check the appropriate blanks)

1. Parent Corporation Name: ____________________
   Mailing Address: ____________________

2. Person to contact regarding information supplied in questionnaire

   Mr/Mrs/Miss ____________________
   Address: ____________________
   Phone ____________

3. If your company manufactures any of the chemicals listed in the cover letter please complete the following form*

	Listed Chemical	Production site-city or town and state
a.		
b.		
c.		
d.		
e.		
f.		
g.		
h.		
i.		
j.		
k.		
l.		
m.		
n.		
o.		

---

*If additional space is needed, please use the back of this sheet.

Listed Chemical (con't.)	Production site-city or town and state (con't.)
p. ________	______________________________
q. ________	______________________________
r. ________	______________________________
s. ________	______________________________
t. ________	______________________________
u. ________	______________________________
v. ________	______________________________
w. ________	______________________________
x. ________	______________________________
y. ________	______________________________

4a. Has any chemical analysis ever been made on any of your products, by-products*, or process waste materials to determine the presence of HCB or HCBD?

HCB ____ yes ____ no HCBD ____ yes ____ no

4b. If the answers are "no", then based on your experience, do you think that any HCB or HCBD may be contained in any of your products, by-products* or process waste materials?

Any HCB ____ yes ____ no Any HCBD ____ yes ____ no

If any of your answers to question 4 are "yes", please complete the remainder of questionnaire; otherwise return questionnaire as completed to this point.

5. Where would the HCB or HCBD occur?

a. In product(s)? ____ yes ____ no

b. In by-product(s)? ____ yes ____ no

c. In process waste materials? ____ yes ____ no

---

*By-products are also referred to as co-products.

6. For each "yes" answer to any category in question 5 please identify compound(s) by name(s) and form(s) (i.e., solid, liquid or gas). Also indicate approximate concentration level(s) and plant location(s).

a. In products

Name(s) and form(s) and plant location(s):

1. ______________________________
2. ______________________________
3. ______________________________
4. ______________________________
5. ______________________________
6. ______________________________
7. ______________________________
8. ______________________________
9. ______________________________
10. ______________________________
11. ______________________________
12. ______________________________

Approximate concentrations levels of HCB and/or HCBD (specify wt. % or ppm)

1.	HCB	____________	HCBD	____________
2.	"	____________	"	____________
3.	"	____________	"	____________
4.	"	____________	"	____________
5.	"	____________	"	____________
6.	"	____________	"	____________
7.	"	____________	"	____________
8.	"	____________	"	____________
9.	"	____________	"	____________
10.	"	____________	"	____________
11.	"	____________	"	____________
12.	"	____________	"	____________

b. In by-products

Name(s) and form(s) and plant location(s):

1. ______________________________
2. ______________________________
3. ______________________________
4. ______________________________
5. ______________________________
6. ______________________________
7. ______________________________
8. ______________________________
9. ______________________________
10. ______________________________
11. ______________________________
12. ______________________________

6b.-continued

Approximate concentration levels of HCB and/or HCBD (specify wt. % or ppm)

1.	HCB		HCBD	
2.	"		"	
3.	"		"	
4.	"		"	
5.	"		"	
6.	"		"	
7.	"		"	
8.	"		"	
9.	"		"	
10.	"		"	
11.	"		"	
12.	"		"	

c. In process waste materials

Name(s) and form(s) and plant location(s):

1. ______
2. ______
3. ______
4. ______
5. ______
6. ______
7. ______
8. ______
9. ______
10. ______
11. ______
12. ______

Approximate concentration levels of HCB and/or HCBD (specify wt. % or ppm)

	Before waste disposal treatment				After treatment (if any)			
1.	HCB		HCBD		HCB		HCBD	
2.	"		"		"		"	
3.	"		"		"		"	
4.	"		"		"		"	
5.	"		"		"		"	
6.	"		"		"		"	
7.	"		"		"		"	
8.	"		"		"		"	
9.	"		"		"		"	
10.	"		"		"			
11.	"		"		"		"	
12.	"		"		"		"	

7. What waste disposal techniques do you use?

Please describe techniques briefly and also comment on their effectiveness in preventing the release into the environment of HCB and HCBD. (e.g., land fill, waste pond, deep well injection, incineration). If incineration is used please indicate operating conditions such as temperature, retention time, gas scrubbing procedure, etc.

8. Please estimate the total amount (lbs/day or lbs/yr) of HCB or HCBD that actually leaves your plant(s):

a. In liquid, gaseous and solid waste streams

b. As impurities in products

c. As a component of by-products

9. To the extent possible within the constraints of proprietary considerations, for each product identified in part 6a please describe briefly the production process used and the approximate annual production:

Product	Process description (e.g. major reactions carried out, or U. S. Patent Number)	Approximate Annual Production Tons

A discussion and summary of the replies to this written inquiry is presented in the following paragraphs.

1. Monsanto Company: Monsanto indicated that in their production of chlorinated biphenyl (Monsanto's only chemical operation of interest to Task I), no detectable concentrations of HCB or HCBD occur in the product or in process waste materials, and that no by-products are produced. In Monsanto's waste disposal operation, scrap liquids containing chlorinated biphenyl are incinerated at about 2700°F for a 1.5 sec retention period and the off-gases are scrubbed to remove hydrogen chloride.

2. Dow Chemical Company: Dow reported that none of their chemical operations pose any HCB or HCBD pollution problems. Dow stated that these toxic materials appear only in their process waste materials and that the total amount of HCB or HCBD emitted from their plants in the form of liquid, gaseous, and solid wastes is too low for an accurate estimate. The process waste materials, principally tars from manufacture of chlorinated solvents, are reported by Dow to be disposed of by a highly effective incineration system.

3. Vulcan Materials Company: Vulcan indicated that HCB and HCBD are contained in their "hex residue" solid waste formed during production of carbon tetrachloride and perchloroethylene, and that all of this waste is impounded in an earth-covered groundfill. Vulcan reported that no HCB or HCBD actually leaves their plant sites.

4. Diamond Shamrock Company: Diamond reported that one of their products, Dacthal®, contains 0.3% HCB and that HCB and/or HCBD occur also in process waste materials from the manufacture of Dacthal®, perchloroethylene, and trichloroethylene. The Dacthal® waste contains about 84% HCB. The company stated that all of the waste materials containing HCB and HCBD are placed in sealed containers and hauled to Rollins International, Inc., in Houston, Texas, for incineration.

5. Ciba-Geigy Corporation: This corporation produces atrazine, propazine and simizine at St. Gabriel, Louisiana (the only domestic production site). Geigy reports that no HCBD is formed, but that HCB occurs in the products and in the waste materials (still bottoms, a liquid residue) and in trace amounts in vent scrubber emissions.

The other four companies did not respond to this written inquiry, even after repeated follow-up requests.

APPENDIX C

PROCEDURE FOR SELECTING MONITORING SITES

Chlorine Plants

There are 65 plants (1973) in the United States which produce chlorine. Some use dimensionally stable anodes (DSAs), some do not. The plants are categorized by the types of cells they employ, and a list showing the 65 plants by cell type is given below.

	Number of Plants	Number Using DSAs	Number Not Using DSAs
Diaphragm cell plants	29	11	18
Mercury cell plants	23	16	7
Diaphragm and mercury cell plants	5	5	0
Fused salt cell plants	4	0	4
HCl electrolysis plants	1	0	1
Diaphragm and fused salt cell plants	1	0	1
Diaphragm and magnesium cell plants	1	0	1
Nonelectrolytic plants	1	0	1
Total	65	32	33

Tables C-I through C-V, which follow, show data which were utilized in selecting monitoring sites from the group of chlorine plants which do not use DSAs. The plants using DSAs do not form HCB or HCBD. The others are considered to be potential emitters of both of these chemicals.

Criteria and Assumptions for Selection of Sampling Sites

(A) Production: Where production figures are grouped, assume each plant produces the same amount of chlorine.

(B) Age of plant: Given--newer is assumed to be cleaner.

(C) Age of cells: Given--newer is assumed to be cleaner.

(D) Types of cells: All Hooker cells have about the same graphite consumption and are considered equal to each other in pollution potential. Dow cells have the same graphite anodes as Hooker cells. The difference is that Dow cells incorporate a multiplicity of unit cells which reduce floor space and investment costs. Columbia cells also have a graphite anode, the difference being that the fingers of the anode extend all the way across the cell.51/

TABLE C-I

NON-DSA PLANTS
(Diaphragm Cells)

	State and City	Producer	Year Built	Cells (Year Installed)	Production (tons/day)
(1)	Baton Rouge, Louisiana	Allied Chemical Corporation	1937	Hooker S-4 (1968)	594 (in 5 plants)
(2)	Syracuse, New York		1927	Hooker S-4 (1968)	
(3)	Wyandotte, Michigan	BASF Wyandotte Corporation	1938	Hooker S-3B	120
(4)	Houston, Texas	Champion International Corporation	1936	Hooker S	Unknown
(5)	Pittsburg, California	Dow Chemical Company	1917	Dow	1,576
(6)	Plaquemine, Louisiana	Dow Chemical Company	1958	Dow	
(7)	Midland, Michigan	Dow Chemical Company	1897	Dow	

TABLE C-I (Concluded)

	State and City	Producer	Year Built	Cells (Year Installed)	Production (tons/day)
(8)	Freeport, Texas	Dow Chemical Company	1940	Dow, (Magnesium)	1,700
(9)	Green Bay, Wisconsin	Fort Howard Paper Company	1968	Hooker S-4	Unknown
(10)	Port Neches, Texas	Jefferson Chemical Company, Incorporated	1959	Hooker S-3B	54
(11)	Gramercy, Louisiana	Kaiser Aluminum and Chemical Corporation	1958	Hooker S-3B	160
(12)	Taft, Louisiana	Hooker Chemical Corporation	1966	Hooker S-4	630 (in 5 plants)
(13)	Tacoma, Washington	Hooker Chemical Corporation	1929	Hooker S-3	
(14)	Barberton, Ohio	PPG Industries, Incorporated	1936	Columbia	1,638 (in 5 plants)
(15)	Corpus Christi, Texas	PPG Industries, Incorporated	1938	Columbia N-1, N-3	
(16)	Henderson, Nevada	Stauffer Chemical Company of Nevada, Incorporated	1942	Hooker S	270 (in 3 plants)
(17)	Newark, New Jersey	Vulcan Materials Company	1961	Hooker S-4 (1968)	153 (in 3 plants)
(18)	Denver City, Texas	Vulcan Materials Company	1947	Hooker S	

TABLE C-II

RECOMMENDATIONS AFTER APPLICATION OF CRITERIA, BY TYPE OF CELLS

Plant No.[a]	Hooker Cells	Recommendation: Based on Criteria
1	S-4	Select: high volume
2	S-4	Eliminate: newer same company as (1)
3	S-3B	Select: high volume
4	S	Select: old, unknown volume
9	S-4	Eliminate: newer
10	S-3B	Eliminate: low volume
11	S-3B	Select: high volume
12	S-4	Eliminate: new, same company as (13)
13	S-3	Select: high volume
16	S	Select: high volume
17	S-4	Eliminate: low volume
18	S	Eliminate: low volume
Plant No.	**Dow Cells**	
5		Eliminate: same as (7) but newer
6		Eliminate: same as (7) but newer
7		Select: older
8		Select: higher volume
Plant No.	**Columbia Cells**	
14		Select: older, high volume
15		Select: older, high volume

---

[a] Referenced to Table C-I.

TABLE C-III

NON-DSA PLANTS
(mercury cells)

State and City	Producer	Year Built	Cells (year installed)	Production (tons/day)
(1) Brunswick, Georgia	Allied Chemical Corporation	1957	Solvay V-100	594 (in 5 plants)
(2) Acme, North Carolina	Allied Chemical Corporation	1963	Solvay V-200	
(3) Linden, New Jersey	Linden Chlorine Products, Inc.	1956	BASF-Krebs(1969)	180
(4) McIntosh, Alabama	Olin Corporation	1952	Olin E-8	524
(5) Augusta, Georgia	Olin Corporation	1965	Olin E-11F	
(6) Niagara Falls, New York	Olin Corporation	1897	Olin E-11F(1960)	
(7) Charleston, Tennessee	Olin Corporation	1962	Olin E-11F, E-812	

Recommendations Regarding Sampling Sites:

Criteria: (A) Production; (B) age of plant; (C) age of cells; and (D) type of cells.

(A) Production is similar for all plants (i.e., 100-200 tons/day).
(B) Only plant built before 1950 was (6).
(C) All cells built after 1950.
(D) Cell types determine the selection. Graphite loss in each type of cell (see Table C-4) is ranked below with the highest graphite consumption cell given first. Higher graphite loss increases the potential for HCB and HCBD formation.

Eliminate: (1), (2), (5), (6), (7) due to cell type.

Recommend: (3) Linden Chlorine Products, Inc., Linden, New Jersey, since it has highest graphite loss and relatively high production, and (4) Olin Corporation, McIntosh, Alabama, second highest graphite loss and oldest cells of group.

TABLE C-IV

NON-DSA PLANTS
(miscellaneous cell types)

State and City	Producer	Year Built	Cells (year installed)	Production (tons/day)
(1) Niagara Falls, New York	E. I. du Pont de Nemours and Company, Incorporated	1898	Downs (fused salt)	122
(2) Memphis, Tennessee	E. I. du Pont de Nemours and Company, Incorporated	1958	Downs (fused salt)	
(3) Baton Rouge, Louisiana	Ethyl Corporation	1938	Downs (fused salt) Hooker S-3D (diaph.)	230
(4) Houston, Texas	Ethyl Corporation	1952	Downs (fused salt)	
(5) Cedar Bayou, Texas	Mobay Chemical Company	1972	Uhde (HCl)	72
(6) Ashtabula, Ohio	RMI Company	1949	Downs (fused salt)	Unknown
(7) Vicksburg, Mississippi	Vicksburg Chemical Company	1962	None	33
(8) Freeport, Texas	Dow Chemical Company	1940	Fused magnesium chloride yields Cl_2 and magnesium	Unknown

Recommendations Regarding Sampling Sites

(A) Eliminate (5) since it is new, has a low production, and involves HCl electrolysis.
(B) Eliminate (7) since it has no cells (nonelectrolytic) and has a very low production.
(C) The remaining six plants are fused salt processes which do not involve carbon. Therefore, eliminate these plants from consideration. Also, they have low production volumes of Cl_2.

Recommended Sample Sites: None

TABLE C-V

GRAPHITE CONSUMPTION/TON Cl_2 FOR DIFFERENT TYPES OF CELLS[50]

	Type of Cell	Graphite Consumed/ Ton Chlorine (lb)
Diaphragm cells:	Hooker S-3B	5.3-7.0
	Hooker S	6.7
Mercury cells:	Solvay V-100 or V-200	3-4
	Olin E-11F	4.8
	Olin E-8F	5.3
	BASF-Krebs	5-6

It appears that the potential for HCB generation is similar for all cells with graphite anodes; but no operating data were found for Dow cells and Columbia cells.

Plants are most conveniently grouped by cell type for comparison. The comparison of plants with similar cells eliminates one variable; cell type.

Production quantity and age of the cells are compared for each plant against the others first, with age of plant considered only if the other two factors are about equal. Production quantity is more important than cell age in this comparison.

Below is a summary of the non-DSA diaphragm cell plants listed in Table C-II that are recommended for further consideration as monitoring test sites.

	Cell Type	Plant Site	Producer
a.	Hooker S-4	Baton Rouge, Louisiana	Allied Chemical Corporation
b.	Hooker S-3B	Wyandotte, Michigan	BASF Wyandotte Corporation
c.	Hooker S	Houston, Texas	Champion International Corporation
d.	Hooker S-3B	Grammercy, Louisiana	Kaiser Aluminum and Chemical Corporation
e.	Hooker S-3	Tacoma, Washington	Hooker Chemical Corporation
f.	Hooker S	Henderson, Nevada	Stauffer Chemical Company of Nevada, Inc.
g.	Dow	Midland, Michigan	Dow Chemical Company
h.	Dow	Freeport, Texas	Dow Chemical Company
i.	Columbia	Barberton, Ohio	PPG Industries, Inc.
j.	Columbia	Corpus Christi, Texas	PPG Industries, Inc.

Final evaluation of recommended diaphragm cell plants: Because of the producers experience in manufacture of toxic chemicals, eliminate: a, b, e, f, g, h, i and j.

Recommended: Plant site monitoring should be considered for Sites c and d.

Carbon Tetrachloride Plants

In 1973, carbon tetrachloride was manufactured at the following plant sites:

Plant No.	Plant Site	Producer	Production Capacity (10^3 tons/year)
1	Moundsville, West Virginia	Allied Chemical Corporation	4
2	Freeport, Texas	Dow Chemical Company	65
3	Pittsburg, California	Dow Chemical Company	22.5
4	Plaquemine, Louisiana	Dow Chemical Company	50
5	Corpus Christi, Texas	E. I. du Pont de Nemours and Company, Inc.	250
6	South Charleston, West Virginia	FMC Corporation	150
7	Le Moyne, Alabama	Stauffer Chemical Company	100
8	Louisville, Kentucky	Stauffer Chemical Company	35
9	Niagara Falls, New York	Stauffer Chemical Company	75
10	Geismar, Louisiana	Vulcan Materials Company	17.5
11	Wichita, Kansas	Vulcan Materials Company	20

Eliminate: Plant 1 because of the very low production capacity. Plants 2, 3, and 4 because Dow incinerates hex wastes in an incinerator which is reported to be highly effective (99.94% destruction of HCB and HCBD).

Plants 6, 7, and 9 because the low temperature (30°C) carbon disulfide process used is not amenable to the formation of either HCB or HCBD. Plant 8 because Stauffer produces HCB and is well aware of the potential hazards of HCB and HCBD.

Recommended monitoring test sites: Plant 5 because it has, by far, the highest production capacity, and it is a new and unproven plant (on-stream since late 1973). Perchloroethylene is a by-product at this Du Pont plant.

Plants 10 and 11 because Vulcan uses landfill operations--with questionable safety--in disposing of hex wastes. Perchloroethylene is also produced at these two Vulcan plants.

Perchloroethylene Plants

In 1973, perchloroethylene was produced at the following plant sites:

Plant No.	Plant Site	Producer	Production Capacity (10^3 tons/year)
1	Deer Park, Texas	Diamond Shamrock Chemical Company	80
2	Freeport, Texas	Dow Chemical Company	60
3	Pittsburg, California	Dow Chemical Company	10
4	Plaquemine, Louisiana	Dow Chemical Company	75
5	Baton Rouge, Louisiana	Ethyl Corporation	25
6	Taft, Louisiana	Hooker Chemical Corporation	25
7	Lake Charles, Louisiana	PPG Industries, Inc.	100
8	Louisville, Kentucky	Stauffer Chemical Company	35
9	Geismar, Louisiana	Vulcan Materials Company	75
10	Wichita, Kansas	Vulcan Materials Company	25

Eliminate: Plant 1 because all wastes containing HCB and HCBD are drummed and hauled off-site to Rollins International, Inc., in Houston, Texas, and incinerated.

Plants 2, 3, and 4 because Dow incinerates the hex wastes in a special incinerator which is claimed to be highly effective (i.e., 99.9+% destruction).

Plant 5 because the production capacity is low and Ethyl has a good plant safety reputation.

Plant 6 because the production capacity is small, and Hooker has experience with toxic chemicals.

Plant 8 because this is a relatively small production capacity, and Stauffer is reported to recover all by-product HCB for sale and to recycle the remainder of the hex material to the process. Therefore, the possibility of HCB or HCBD entering the environment is slight.

Recommended monitoring test sites: Plants 7, 9, and 10.

Plant 7 is recommended because it has the highest production capacity and was reported to have used a landfill operation (which is not considered to be a safe method for disposal) until completion of an incinerator in 1973.

Plants 9 and 10 are recommended because landfill operations are used for disposal of hex wastes.

Trichloroethylene Plants

In 1973, trichloroethylene was produced at the following plant sites:

Plant Site	Producer	Production Capacity (10^3 tons/ year)
Deer Park, Texas	Diamond Shamrock Chemical Company	50
Freeport, Texas	Dow Chemical Company	75
Baton Rouge, Louisiana	Ethyl Corporation	25
Taft, Louisiana	Hooker Chemical Corporation	20
Lake Charles, Louisiana	PPG Industries, Inc.	140

The hex wastes from trichloroethylene production are disposed of in the same manner as the hex wastes from perchloroethylene production. In each case, the trichloroethylene plants are operated in conjunction with a perchloroethylene operation at a common plant facility. The Lake Charles, Louisiana, site of PPG Industries, Inc., is recommended for on-site monitoring because of the very large production capacity.

Vinyl Chloride Monomer

Vinyl chloride monomer was produced in 1973 at the following plant sites:

Plant Site	Producer	Production Capacity (10^3 tons/year)
Baton Rouge, Louisiana	Allied Chemical Corporation	150
Long Beach, California	American Chemical Corporation	87.5
Westlake, Louisiana	Continental Oil Company	325
Freeport, Texas	Dow Chemical Company	100
Oyster Creek, Texas	Dow Chemical Company	350
Plaquemine, Louisiana	Dow Chemical Company	195
Baton Rouge, Louisiana	Ethyl Corporation	150
Pasadena, Texas	Ethyl Corporation	75
Calvert City, Kentucky	B. F. Goodrich	500
Geismar, Louisiana	Monochem, Inc.	150
Lake Charles, Louisiana	PPG Industries, Inc.	200
Deer Park, Texas	Shell Chemical Company	420
Norco, Louisiana	Shell Chemical Company	350
Houston, Texas	Tenneco, Inc.	112.5
Texas City, Texas	Union Carbide Corporation	75
Painesville, Ohio	Uniroyal, Inc.	NA

The technical literature and inquiries to industry spokesmen indicate a potential for the formation of HCB. Spokesmen from Dow Chemical Company and from Ethyl Corporation have indicated that no HCBD is formed in the manufacture of vinyl chloride. Vinyl chloride is commonly produced from ethylene dichloride, which in turn is made from ethylene.

Based on the limited data collected concerning the composition of the tarry wastes in this industry, MRI has estimated that significant quantities of HCB could be formed in the manufacturing operations and contained in these tarry residues.

On the basis of this evaluation one representative vinyl chloride monomer plant was selected for inclusion in the list of recommended monitoring test sites. The selected site is the Lake Charles, Louisiana, facility of PPG Industries. This is a large production capacity plant (200 x 10^3 tons/year).

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